

**THE IN-PLACE
POLLUTANTS PROGRAM**

VOLUME VII

**A SYNTHESIS
OF THE PROGRAM**

FEBRUARY 1992



Ontario

**Environment
Environnement**

92-04810/

ISBN 0-7729-9040-9 (2 Pt. Set)
ISBN 0-7729-9041-7

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FEBRUARY 1992



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PIBS 1838E01

ACKNOWLEDGMENT

The authors gratefully acknowledge the assistance of Mr. W. Scheider and Dr. G. Krantzberg of the Ministry of the Environment, in reviewing the draft report and providing valuable suggestions. Special thanks are given to staff from Laboratory Services Branch for analyses of sediment samples. Biota tissue residues were provided by OceanChem Ltd. and Enviroclean under contract to the Ministry.

Financial assistance and technical advice were provided by Environment Canada through the Polluted Sediment Committee of the Canada-Ontario Agreement. These contributions are gratefully acknowledged.

FOREWORD

In 1983, the Ministry of the Environment initiated the In-Place Pollutants program in response to various concerns related to potential impacts of contaminants in sediment on the aquatic ecosystem. The major objective of the program was:

"To determine the potential impacts of contaminants in sediment on overlying water quality and on aquatic biota with the aim of developing strategies for the management of contaminated sediment".

The various studies launched towards achieving this objective have been reported in a series of In-Place Pollutants publications covering six volumes.

This report, Volume VII in the series, summarizes the findings of the In-Place Pollutants studies and puts these findings in perspective with concurrent work of other research published in the literature. The combined information forms the basis of the conclusions outlined in this report.

SUMMARY AND CONCLUSIONS

Through the In-Place Pollutants Program, it was possible to examine various developing and proven techniques for assessing the impacts of contaminants in sediment on the aquatic ecosystem. Based on the results obtained, it is now possible to identify certain approaches that can be adopted to provide usable information for informed decisions regarding the management of contaminated sediments.

Major benefits of the program were realized in the following areas:

1. The data collected has been a major source of information in developing sediment quality guidelines (Provincial SQGs)
2. The program also lead to the development of a bioassay protocol for determining the toxicity of sediments and to the set-up of a testing laboratory for this analysis.
3. The program provided a better understanding of sediment contaminant problems which is essential to making informed decisions on managing contaminated sediments.

The following conclusions were drawn from the data obtained:

1. It is difficult to establish any impact from sediment to the overlying water. Because of continuing external sources in many of the areas studied, and the overwhelming dilution capacity of the overlying water for any material released from sediment, the significance of the sediment source is not apparent in the areas studied.
2. Bulk sediment chemistry continues to be an essential measure of the degree and extent of sediment contamination. Bulk sediment chemistry also provides useful indications of spatial and temporal trends in contaminant accumulation.
3. Sequential extraction of metals in various geochemical fractions of sediment at this stage of their development and understanding provide little information above that gained from bulk chemistry that is of any immediate significance in assessing sediments.
4. Tissue analysis of benthic organisms provides useful information on contaminant uptake even though the specific mechanisms of uptake are still unclear. The use of higher organisms such as sculpins proved less useful as a gauge for sediment due to the large number of variables that can influence uptake.
5. Benthic community analysis studies provide a good measure of response at the population and community levels and have been shown in this and other studies to respond to the changing characteristics of their environment. These studies are most effective in measuring the general ecosystem health.
6. Laboratory bioassays provide a useful measure of the effects of sediment contamination on benthic and water column organisms. However, there are many inherent difficulties associated with laboratory assays, especially with regard to extrapolating such information to field settings.
7. The distribution of contaminants in sediment varies considerably across the province. In the most seriously contaminated areas, chemical contamination occurs in conjunction with high levels of organic matter and accumulation appears to be a result of the eutrophication of water bodies that accompanies settlement and urbanization. It is difficult in most cases to separate the effects of the organic matter from the chemical contaminants on aquatic life.
8. Most sediments with high levels of contamination are impacted by active sources of discharge. In certain areas, high metal levels originate from natural sources. In future studies, such areas must be clearly identified in order to make sensible management decisions. In general, the levels of organic contaminants were low except for persistent organics such as PCBs and PAHs in certain areas.

In fulfilment of the objectives of the program, work in the following areas is ongoing:

1. Development and refinement of laboratory bioassays and procedures for relating laboratory information to field conditions.
2. Development of mechanistic models to determine the movement of contaminants once the relationships between sediment contamination, water column concentrations and tissue residues in biota have been quantified.
3. Development of a standard protocol to assess field conditions, i.e. a standard series of assessment procedures by which we can gather acceptable data.
4. Development of criteria for remediation of areas of contaminated sediment and the setting of suitable ecological targets for remediation.
5. Development of Provincial Sediment Quality Guidelines for those compounds, such as the PAHs, that have been found to accumulate in sediments and are causes for potential concern.

The In-Place Pollutants Program to date has focused primarily on the Great Lakes. The demonstrated usefulness of this approach now suggests that this integrated study approach could be expanded to include the assessment of all provincial waters and that this type of study should be incorporated into a wide range of assessment activities.

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I INTRODUCTION

The long-standing view of sediments as merely sinks for contaminants has, over the last 10 years, given way to the recognition that they can also be a significant source of contaminants to the water column and water column organisms, as well as to those organisms that live in direct contact with the sediments. In determining the fate and movement of contaminants, consideration must be given not only to the sediments themselves, but also to the overlying water and the aquatic biota. The determination of the effects of contaminants needs to consider not just such traditional measurements as changes in species composition, but also the chronic effects (long term) of uptake of these contaminants. Some of the more complex issues surrounding contaminated sediments relate to their contribution to organism tissue residues.

The knowledge that sediments are not a separate system, but rather, form an integral part of the aquatic ecosystem, has been at the foundation of the development of a holistic or ecosystem approach to the study of sediment and sediment contaminant problems. This, in turn, has brought about an increased awareness of the need to study the physical, chemical and biological characteristics of contaminated sediment problem areas as an integrated whole. This approach formed the basis of the MOE's In-Place Pollutants Program (IPP), launched by the Ministry in 1983 and completed in this volume. While past methods of contaminant evaluation have involved most of the techniques employed in the In-Place Pollutants Program, few of these studies have attempted to relate changes or effects in one part of the ecosystem (sediments, for example) with impacts on another (such as the water column). It is no longer sufficient, for example, to look at the benthic communities of lakes without considering the observed community changes in relation to the sediment, water column and biological assimilation. Similarly, while contaminant uptake has been measured, these have seldom been related to the physical and chemical characteristics of the sediment. Yet, the type of sediment can play a major role in the sorption of contaminants and their availability to organisms. The ecosystem approach has, as a result, necessitated both the development and evaluation of new techniques, such as sediment geochemical extraction procedures, and the re-evaluation of existing methodologies.

The major objectives of the MOE In-Place

Pollutants program were to determine the extent of contaminated sediment problems in the province and to assess the potential impacts of contaminants in sediment on overlying water quality and on the aquatic biota. This information was subsequently used to assess the nature of the relationships among the different environmental compartments. The ultimate aim was to make use of this information to aid in the development of strategies for the management of contaminated sediment. This included both the development of protocols for laboratory and field studies and beyond that, using the information to assist in deriving measures to protect the environment. The most significant of these to emerge from the program have been the Provincial Sediment Quality Guidelines and the development of a sediment bioassay protocol.

The extent of sediment contamination problems in Ontario is significant. While past attention has focused on contaminants in the water column, there is a recognition that these may only be a transient problem. Ultimately, most of the contaminant load to the water that is not lost through volatilization, dissociation, or transformation is deposited in the bottom sediments. Hence, bottom sediments can be significant reservoirs for contaminants. Eisenreich (1988) for example, found that the distribution of PCB in Lake Superior was approximately evenly divided between the sediments and the water column (ca. 10,000 kg in each). Considering the much larger volume of water than sediment, the sediment bound PCBs represent a significant reservoir of contaminants.

The In-Place Pollutants Program was begun in 1983 and at the termination of the field component in 1987, a total of 326 stations from 20 different localities had been sampled (Figure 1; Table 1). Sampling sites included areas identified by the IJC as Areas of Concern (e.g. Hamilton Harbour, Toronto Waterfront, St Mary's River) and later, as MISA pilot sites (e.g., Grand River, Toronto Main STP). All sites were chosen on the basis of known or anticipated sediment contamination.

The program undertook to assess contaminated sediments from an ecosystem perspective. The study sought to assess the extent and severity of sediment contamination through chemical analysis of the sediments, and to relate these findings to effects on the water column and aquatic organisms. Thus, sediment assessment included not only chemical analysis of the sediments, but also analysis of the biota resident in the sediment, such as benthic invertebrates, and those organisms feeding on or

Table 1: Study Locations and Number of Areas Sampled

Study Location	1983	1984	1985a	1985b	1986	1987
Toronto Harbour and Waterfront	42		20	27		12
Hamilton Harbour	10					
Frenchman's Bay	5					
Oakville Harbour				9		
St Catharines				6		
Penetang Harbour				10		
Midland Bay				10		
Bay of Quinte				10		
Wheatley Harbour			3			
Detroit River		8		10		
Niagara River				8		
St. Clair River	8	8		10	9	
St. Mary's River	8		5	10		7
Kam River					9	
St. Lawrence River:						
Kingston	5					
Maitland		4				
Cornwall					10	
Collingwood Harbour					19	
Grand River						3
Canagagigue Creek						6
Rice Lake/Otonabee River						14
Totals	78	20	28	111	47	42

near the sediment surface, such as bottom feeding fish. Additionally, effects on the water column were included in order to determine whether sediment contamination had any discernible effect on water quality. This question was of considerable importance, since sediments have the potential to become a major source of contaminants once effective

source control has been achieved.

The sediment chemical parameters studied included the metals (Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn), pesticides (Table 2) and PCBs. Additional parameters, such as chlorophenols, PAHs and a variety of chlorinated aromatics were

Table 2: Contaminants Analysed in the In-Place Pollutants Program.

PCB/ Organochlorine Pesticides	Aldrin, α -BHC, γ -BHC, α -chlordane, γ -chlordane, dieldrin, DMDT, endosulfan-I, endosulfan-II, endrin, endosulfan sulphate, heptachlor, heptachlor epoxide, mirex, oxychlordane, o,p - DDT, p,p -DDD, p,p -DDE, p,p -DDT, PCBs, HCB, OCS, hexachloroethane, HCBd.	1985 through 1987
PAHs	Phenanthrene, anthracene, fluoranthene, fluorene, pyrene, benzo[a]anthracene, chrysene, benzo[e]pyrene, benzo[fluoranthene, perylene, benzo[a]pyrene, benzo[g,h,i]perylene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene, benzo[b]chrysene, coronene, naphthalene, dimethylbenz[a]anthracene, acenaphthene, acenaphthylene, dioanthracene.	1986, 1987
Chlorinated Aromatics	1,2,3 trichlorobenzene, 1,2,4-trichlorobenzene, 1,2,3-trichlorobenzene, 2,4,5-trichlorotoluene, 2,3,6-trichlorotoluene, 2,6,a-trichlorotoluene, 1,2,3,5-tetrachlorobenzene, 1,2,4,5-tetrachlorobenzene, 1,2,3,4-tetrachlorobenzene, pentachlorobenzene.	1986, 1987
Chlorophenols	2,3,4-trichlorophenol, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, 2,3,4,5-tetrachlorophenol, 2,3,5,6-tetrachlorophenol, pentachlorophenol.	1986, 1987
Metals	Aluminum, arsenic, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, zinc.	1983 - 1987
Other Parameters	pH, Eh, total organic carbon, loss on ignition, phosphorous, total kjeldahl nitrogen, oils and greases, grain size.	1983 - 1987

added in 1985, though these were added selectively and usually only at those sites where contamination was suspected. Table 2 lists the parameters analyzed at each site during each sampling year.

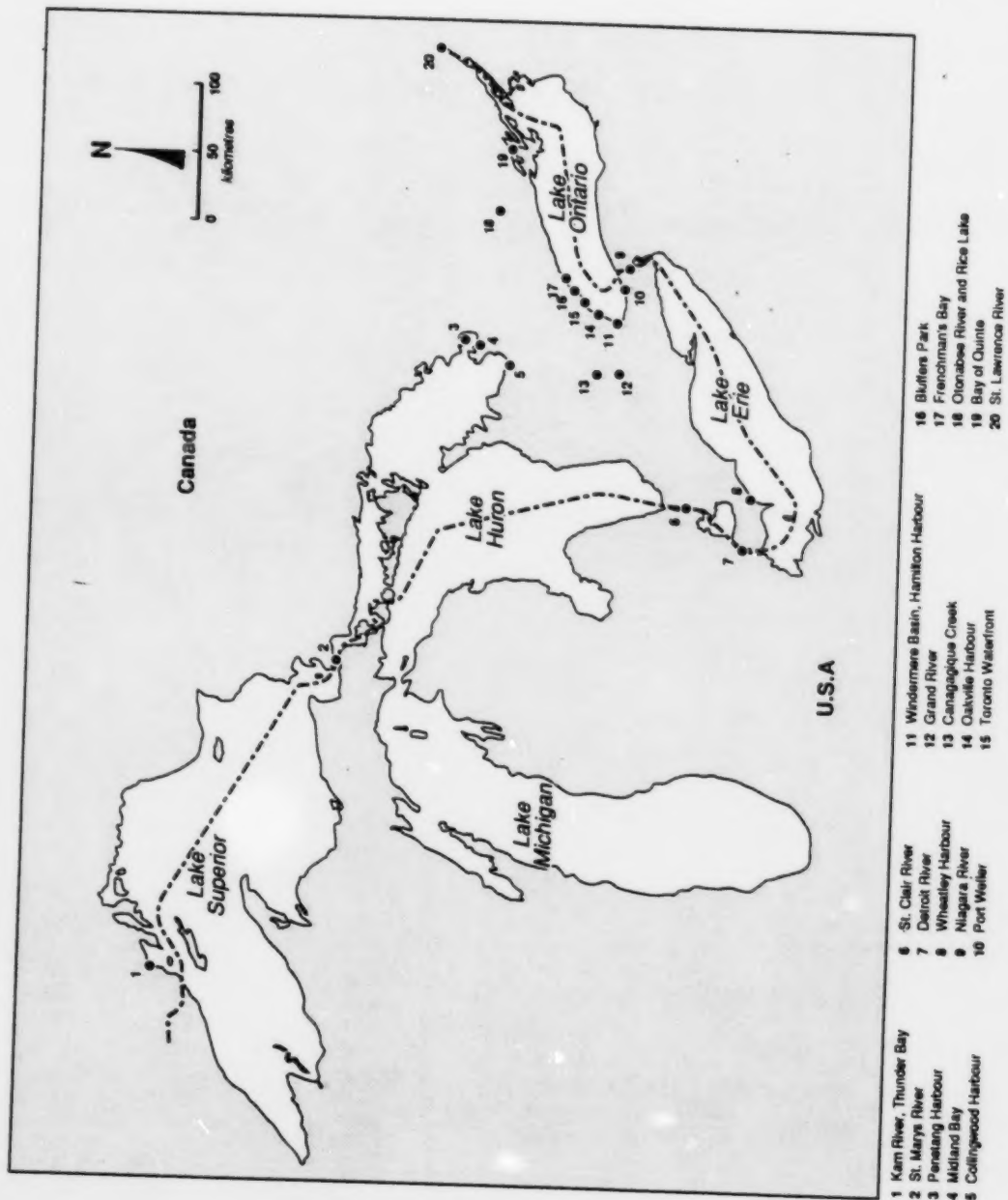
Benthic organisms and bottom feeding fish were also analyzed for metals, pesticides and PCB residues in tissues. At certain sites, tissues were also analyzed for chlorophenols and PAHs.

Benthic organism community analysis was undertaken at all sites, commencing in 1985, to assess the general effects of contaminated sediments on the *in situ* organisms.

Laboratory testing of field-collected sediments, using a benthic species (*Hexagenia*) and a water column species (Fathead minnows) was added in 1986, once acceptable protocols had been developed. The bioassay assessed the relative toxicity of the sediments on aquatic organisms.

Figure 1

**In-place Pollutants Program
Location of study sites, 1983 - 1987**



II MAJOR FINDINGS

1. Sediments

1.1 Significance of Contaminants in Sediments - Theoretical Considerations

Sediments are often the primary reservoir or sink for most contaminants discharged to the water. Most metals and organic compounds tend to bind or partition to particles (mainly organic particles) in the water column and subsequently settle to the bottom (Sigg *et al.* 1987; Smith *et al.* 1988). The concentration of contaminants in sediments is therefore a reflection of contaminant concentrations from all sources. Their distribution, in turn, is governed by many factors, such as current and wave action, suspended particle concentration and sorption characteristics.

Since sediments play a substantial role in the fate of contaminants, the physical and chemical characteristics of the sediments are of major concern. The composition of the sediments appears to be the single most important factor affecting contaminant accumulation. At the most basic level, however, contaminant interactions with sediment components depend on the nature of the contaminants. Most contaminants can be placed in one of two major groups; ionizable compounds and non-ionizable compounds. In water, the ionizable compounds dissociate into an anion and a cation, which are then able to react with other ions. The non-ionizable compounds are extremely stable and do not dissociate. Ionizable contaminants (the metals as well as some, generally non-persistent organic compounds) behave in a more complex fashion than non-ionizable (hydrophobic) organic compounds.

1.2 Metal Behaviour in Sediments

1.2.1 Theoretical Considerations

Metals are a basic part of the earth's geochemistry and occur naturally in all environments principally through the weathering of mineral-rich rock. Metals can also originate from anthropogenic sources and these include virtually all man-made sources that release metals to water-courses or the atmosphere.

Because metals ionize in water, they are able to

form a variety of different types of compounds with various complexing ligands. Furthermore, the types of complexes formed and the types of complexing ligands can change, not only from one area to another, but also within the same area. The forms that a metal occurs in at the sediment surface, where generally aerobic conditions prevail are usually different from those forms that occur at depth in the sediments, particularly under anoxic (anaerobic) conditions.

A number of compounds or groups of compounds generally account for most of the metal complex formation in sediments. Some of these are important sinks for metals, such as organic carbon and sulphides, while others may act as both sinks and sources (i.e. act as reservoirs) depending on sediment chemical conditions. The latter include complexes formed with Fe/Mn oxides which, under the appropriate sediment conditions, can release previously complexed metals into solution.

The most important factor governing the complexation of metals in sediments appears to be oxygen. The changes in sediment redox potential that result as conditions change from oxic to anoxic can affect the availability of metals from sediments, with potential impact on toxicity and bioaccumulation. Additional factors that may enhance or decrease availability include changes in the sediment pH and the presence of complexing ligands.

Changes in sediment redox potential, in particular, can affect the binding of contaminants to specific sediment fractions. For example, a change from oxic to anoxic conditions can result in release of metals previously bound to the Fe/Mn oxide fraction as these dissolve under anoxic conditions. Thus, in most cases the sediments cannot be considered as a permanent sink for contaminants, but merely as a reservoir, storing the metal until conditions favour their release. In most fine-grained sediments in depositional zones of lakes, the depth of oxygen penetration is low and the change from oxic to anoxic conditions occurs within the first few centimetres. Below this depth, decomposition processes in the sediment that consume oxygen generally outpace the diffusion rate of oxygen from the overlying water. Thus, only at the sediment surface do chemical processes operate under oxic conditions.

Changes in redox potential as sediments become anoxic can also result in the formation of metal sulphides. In sulphide-rich sediments many metals, upon release from the Fe/Mn hydroxides,

will form insoluble sulphides. Provided the sediment is not disturbed, these metals are not released but are effectively removed from the system (i.e. a true sink). Sulphides, however, are not the only factor controlling metals in anoxic sediments. Sakata (1985) found no release of Cu and Pb from pond sediments under anoxic conditions, despite significant release of Fe and Mn. Since no sulphide was detected in these sediments, they postulated that some other mechanism must be removing the released metal ion.

Brook and Moore (1988) found that in sediments, enriched cadmium, copper, manganese and zinc were primarily in the reducible (approx. F2 + F4 fractions) and the organic/sulphide (F3) fractions, with relatively smaller amounts in the residual fraction. In contrast, Fe and Ni occurred primarily in the residual fraction.

Moore *et al.* (1988) noted that while under anoxic conditions sulphides may effectively remove metals through complexation, if these sediments are removed from the reducing environment and exposed to oxygen, the sulphides would oxidize and release metals (especially copper and zinc) and arsenic. *This of course has implications for any marine construction projects that entail the removal or relocation of highly contaminated sediments. Similarly, it could result in release of contaminants from sediments located in areas exposed to other physical disturbances, such as storm activity or ship traffic that could result in resuspension of sediment.*

Redox changes in the sediments that result in release of metals to water or the porewater, or that result in a change in the complexing ligand, can have implications for biota as well. The release of metals to the porewater can heighten the availability of the metals and increase the potential for uptake. In addition, the toxicity of a number of metals is dependent on their oxidation state i.e., certain oxidation states of some metals are more toxic than others. Di Toro *et al.* (1990) observed that for a number of metals the divalent state was the most toxic to organisms. Mok and Wai (1990) found that at the natural pH of most waters (i.e. below 8.0) As(III) was the dominant form (probably as $H_2AsO_3^-$), a form which is relatively mobile. Similar behaviour has been noted for numerous other metals (Stumm and Morgan 1981).

For most metals, the sediment constituents to which they will bind or partition cannot be predicted. Luoma (1986) found that Cu was predominantly partitioned to organic matter in some

sediments while it partitioned mainly to other components (Fe/Mn oxides/hydroxides) in other sediments and that the differences were related to the relative abundances of the specific components.

Changes in sediment conditions can also result in changes in the binding of metals, with the result that metals in sediments are not static over time. Mok and Wai (1990) suggest that those metals with a strong affinity for the Fe/Mn oxides/hydroxides can, as the oxides redissolve in anoxic sediments, migrate upward through the sediments to be immobilized once again through coprecipitation with the Fe/Mn oxides in the oxic surface layer or bottom water. It can be postulated, therefore, that metals could migrate upward through the sediment, resulting in higher surficial sediment concentrations that may not necessarily be due to recent deposition from the water column.

Disturbance of sediments by the organisms inhabiting the sediment (bioturbation) can also affect the release of contaminants, especially in organically enriched areas where population densities may be extremely high. Boddington *et al.* (1979) found that the burrowing activity of tubificid oligochaetes resulted in a significant flux of mercury from the top 1 cm of sediment. Starkel (1985) observed that the predicted flux rate of iron from sediments with average densities of organisms was enhanced twofold over the predicted flux for diffusion alone. Riedel *et al.* (1989) found a measurable flux of arsenic out of sediments when burrowing animals were present, which was not measured in the absence of organisms. Other studies (Fisher *et al.* 1980) have also found that bioturbation can result in significant quantities of sediment being moved to the sediment surface. The impacts can be significant locally, since the sites of the severest sediment contamination are often the sites of highest organic matter content and usually have extremely high densities of sediment-dwelling organisms as well. Thus, the potential for release of significant quantities of material from sediment increases greatly in areas of high benthic productivity.

The specific effects of all of the factors affecting the fate and transport of metals in sediments will of course vary from area to area, with the result that release to the water column, interstitial water, or availability to aquatic organisms will not be the same from one site to another. Evidently, the complex behaviour of metals in sediments suggests that our ability to develop predictive mechanisms to explain their behaviour is not encouraging given the

present state of knowledge.

1.2.2 Program Synthesis - Distribution of Metals

During the course of the In-Place Pollutants program, sediment samples from a total of 308 stations (analyses were not performed at all stations) were analyzed for metal content. Throughout the study sites, the accumulation of metals in sediment show a strong and predictable association with centres of urbanization and industrialization. Bulk sediment concentrations of all metals increased in the most highly industrialized areas. The study has also found that metals in sediments tend to accumulate to higher concentrations in areas of high organic matter accumulation.

Organic enrichment of sediments also tends to be highest in urban areas, primarily as a result of historic discharges of organic wastes, of which sewage and erosion are the principal sources. The result is that metals and organic matter have tended to co-accumulate in sediments, and, given the affinity of metals for organic particles, as noted in the previous section, this co-accumulation is not surprising. In some cases accumulation of organic matter has occurred through alteration of the shoreline as a result of lakefill construction projects which have altered water movement by interruption of existing current and wave patterns. These structures have also created numerous embayments and the resulting low energy environments have facilitated the accumulation of fine-grained material in these protected areas (D. Wilkins, Pers. Comm.).

The IPP sites were ranked from most contaminated to least contaminated area for each of the parameters measured (Appendix, Tables 1a-1c). For the metals copper, chromium, mercury, lead, zinc, nickel and cadmium, the Toronto Harbour, Humber Bay, Ashbridges Bay, Hamilton Harbour (Windermere Basin) and the Detroit River were the most contaminated areas. Bulk sediment metal concentrations exceeded the Severe Effect Level (SEL) of the proposed Provincial Sediment Quality Guidelines at these locations and these areas can be considered as seriously contaminated (Figures 2, 3, 4, 5 and 6). Humber Bay had the greatest number of exceedances (Figure 3) with Cu, Cr, Cd, Ni and Zn all in excess of the Severe Effect Level guidelines. Windermere Basin (Hamilton Harbour) sediments exceeded the guidelines for Cu, Cr, Pb, and Zn (Figure 2). However, on the basis of a simple index, calculated as:

$$\frac{\sum [X] \text{ in sediment}}{\text{S.E.L. of X}} + \frac{[Y] \text{ in sediment}}{\text{S.E.L. of Y}} \dots$$

Windermere Basin sediments exceeded the SEL guidelines by the greatest amount (Table 4). (The index was calculated as the sum of all exceedances of the Severe Effect Level guidelines for all metals (i.e. sediment concentration / SEL guideline)).

The highest sediment concentrations for Cu, Cr and Zn were recorded in the Windermere Basin while Ashbridges Bay, Toronto Harbour and the areas surrounding the East Headland exceeded the SEL guidelines for fewer parameters and by lesser amounts. However, Toronto Harbour had the highest sediment lead concentrations, while mercury concentrations were highest in Ashbridges Bay.

Table 3: Percentage of Stations Exceeding the Provincial Sediment Quality Guidelines.

METAL	Above L.E.L.	Above S.E.L.
Arsenic	21	0
Cadmium	49	3
Chromium	59	13
Copper	75	10
Mercury	34	2
Iron	40	4
Manganese	28	2
Nickel	48	2
Lead	56	6
Zinc	42	3

Iron and manganese, in contrast, were highest in the St Mary's River and the Detroit River, exceeding the SEL guidelines at a number of stations (Fig 5 and 6). The exceedance of the Severe Effect Level has serious implications for aquatic organisms, since the level is denoted as the sediment concentration that can adversely affect all but the most tolerant benthic organisms.

The study sites were considered on the basis of the percentage of stations that exceeded the Severe Effect Level and the Lowest Effect Level. These results are presented in Table 3.

Despite the accumulation of high

Table 4: Index of Total Severe Effect Level Exceedances for Metals at In-Place Pollutants Sites, 1983 to 1987.

Rank	Location	Year	Stn	SELScore	Rank	Location	Year	Stn	SELScore
1	Hamilton Harb.	83	2089	20.13	51	East Headland	85	1391	4.25
2	Humber Bay	85	2335	17.4	52	St Mary's R.	83	49	4.19
3	Detroit River	85	85	15.12	53	Humber Bay	84	2727	4.17
4	Hamilton Harb.	83	2090	14.17	54	Niagara River	85	145	4.16
5	Toronto Main	87	8	13.42	55	Penetang Harb.	85	530	4.09
6	Hamilton Harb.	83	2086	12.59	56	East Headland	83	2284	4.08
7	Detroit River	85	103	11.75	57	Kam River	86	6	4.05
8	Humber Bay	85	2332	11.71	58	St Mary's R.	85	45	4.04
9	Toronto Harb.	85	1360	11.49	59	Niagara River	85	113	4.01
10	Humber Bay	83	2115	11.45	60	Kam River	86	2	4
11	Hamilton Harb.	83	2088	10.92	61	Midland Bay	85	512	3.96
12	Detroit River	85	62	9.98	62	St Mary's R.	87	2	3.91
13	St Mary's R.	87	5	9.6	63	Rice Lake	87	14	3.9
14	Ashbridges Bay	83	2034	8.43	64	Kam River	86	8	3.81
15	Humber Bay	83	2370	8.31	65	Detroit River	85	101	3.81
16	Ashbridges Bay	85	2034	7.85	66	Kam River	86	5	3.78
17	Toronto Harb.	85	1346	7.66	67	Toronto Harb.	83	1379	3.76
18	Frenchman's Bay	83	2091	7.6	68	Midland Bay	85	521	3.71
19	St Mary's R.	85	48	7.58	69	Humber Bay	83	2118	3.65
20	Hamilton Harb.	83	2087	7.1	70	Penetang Harb.	85	522	3.63
21	Humber Bay	83	2331	6.96	71	Kam River	86	11	3.59
22	St Mary's R.	87	1	6.77	72	Penetang Harb.	85	529	3.53
23	St Mary's R.	87	4	6.68	73	Humber Bay	84	2721	3.51
24	St Mary's R.	85	47	6.43	74	Port Weller	85	2472	3.49
25	Humber Bay	83	2368	5.97	75	Rice Lake	87	12	3.47
26	St Mary's R.	85	49	5.9	76	Niagara River	85	155	3.44
27	Toronto Harb.	83	1357	5.9	77	Humber Bay	83	2340	3.41
28	Toronto Harb.	83	1352	5.8	78	Humber Bay	85	2113	3.4
29	Toronto Harb.	83	1366	5.77	79	Kam River	86	1	3.34
30	Toronto Harb.	83	1354	5.71	80	Humber Bay	83	2371	3.33
31	St Mary's R.	83	48	5.7	81	Rice Lake	87	3	3.29
32	Toronto Harb.	83	1346	5.69	82	Humber Bay	84	2720	3.22
33	Toronto Harb.	83	1365	5.35	83	St Lawrence R.	86	369	3.2
34	Humber Bay	83	2335	5.29	84	Humber Bay	83	2369	3.15
35	Ashbridges Bay	84	2715	5.2	85	Oakville Harb.	85	2840	3.14
36	Ashbridges Bay	84	2711	5.18	86	Midland Bay	85	518	3.12
37	St Mary's R.	87	7	5.17	87	Frenchman's Bay	83	2092	3.11
38	Toronto Harb.	85	1363	5.15	88	Rice Lake	87	6	3.1
39	Detroit River	85	70	5.03	89	Kam River	86	3	3.09
40	Ashbridges Bay	84	2716	5.02	90	St Lawrence R.	86	375	3.02
41	Humber Bay	84	2718	5.01	91	Humber Bay	84	2726	3.01
42	Humber Bay	84	2728	4.99	92	Rice Lake	87	9	3.01
43	Humber Bay	84	2724	4.92	93	St Mary's R.	85	75	3.01
44	Humber Bay	84	2729	4.87	94	Collingwood H.	86	21	3
45	Humber Bay	83	2113	4.8	95	Rice Lake	87	11	2.99
46	Humber Bay	84	2722	4.79	96	Toronto Harb.	83	1375	2.96
47	St Mary's R.	83	46	4.6	97	East Headland	83	2277	2.96
48	Toronto Harb.	83	1371	4.46	98	Humber Bay	84	2725	2.96
49	Toronto Harb.	83	1362	4.45	99	Oakville Harb.	85	2844	2.93
50	East Headland	85	1389	4.42	100	Kam River	86	18	2.92

Table 4: cont'd.

Rank	Location	Year	Stn	SELScore	Rank	Location	Year	Stn	SELScore
101	Humber Bay	85	2363	2.9	152	Oakville Harb.	85	2846	2.12
102	Niagara River	83	157	2.84	153	Collingwood H.	86	20	2.11
103	Midland Bay	85	519	2.82	154	Toronto Main	87	9	2.11
104	Humber Bay	83	2367	2.81	155	Detroit River	85	100	2.09
105	Kam River	86	17	2.78	156	East Headland	85	2282	2.09
106	Oakville Harb.	85	2841	2.75	157	Bluffers Park	84	2707	2.08
107	St Lawrence R.	86	373	2.75	158	Bluffers Park	83	2083	2.07
108	Grand River	87	2	2.7	159	St Clair R.	83	69	2.04
109	Humber Bay	85	2355	2.66	160	Frenchman's Bay	83	2094	2.03
110	St Mary's R.	83	47	2.64	161	Hamilton (outer)	83	2099	
111	Humber Bay	84	2723	2.62	162	Hamilton (outer)	83	2098	
112	Hamilton (outer)		83	2100	163	Rice Lake	87	7	1.98
113	Penetang Harb.	85	523	2.61	164	Toronto Main	87	5	1.97
114	Humber Bay	83	2334	2.57	165	Bluffers Park	84	2704	1.96
115	Midland Bay	85	513	2.56	166	Bluffers Park	84	2511	1.94
116	Humber Bay	83	2330	2.56	167	Toronto Main	87	6	1.88
117	Grand River	87	3	2.52	168	Toronto Main	87	1	1.87
118	Frenchman's Bay	83	2095	2.52	169	East Headland	83	2280	1.86
119	Detroit River	85	102	2.5	170	Collingwood H.	86	22	1.84
120	Penetang Harb.	85	524	2.49	171	Niagara River	83	127	1.82
121	Humber Bay	83	2337	2.49	172	Midland Bay	85	516	1.82
122	Collingwood H.	86	23	2.49	173	St Clair R.	86	218	1.81
123	St Lawrence R.	86	371	2.48	174	Humber Bay	85	2352	1.8
124	Midland Bay	85	515	2.45	175	Collingwood H.	86	30	1.79
125	Niagara River	83	156	2.43	176	Canagagigue Ck	87	1	1.77
126	St Lawrence R.	86	374	2.41	177	St Lawrence R.	86	366	1.74
127	Midland Bay	85	517	2.4	178	Niagara River	83	160	1.72
128	Humber Bay	83	2336	2.39	179	Bluffers Park	84	2702	1.7
129	Midland Bay	85	514	2.39	180	Port Weller	85	2444	1.7
130	Toronto Main	87	12	2.38	181	Canagagigue Ck	87	2	1.68
131	Hamilton (outer)		83	2096	182	East Headland	85	2108	1.67
132	Rice Lake	87	10	2.36	183	St Mary's R.	87	6	1.64
133	St Lawrence R.	86	362	2.36	184	Toronto Main	87	11	1.64
134	St Lawrence R.	86	368	2.35	185	St Clair R.	86	34	1.63
135	Rice Lake	87	1	2.34	186	Canagagigue Ck	87	6	1.62
136	Oakville Harb.	85	2845	2.34	187	Humber Bay	85	2367	1.58
137	Penetang Harb.	85	528	2.29	188	Toronto Main	87	3	1.58
138	Niagara River	83	183	2.28	189	Midland Bay	85	520	1.57
139	Canagagigue Ck	87	5	2.28	190	Oakville Harb.	85	2843	1.57
140	Rice Lake	87	8	2.27	191	Toronto Main	87	7	1.56
141	East Headland	83	2373	2.25	192	Oakville Harb.	85	2847	1.54
142	Rice Lake	87	2	2.24	193	Humber Bay	84	2719	1.52
143	Port Weller	85	2440	2.23	194	Niagara River	85	177	1.51
144	St Lawrence R.	86	372	2.21	195	Detroit River	85	104	1.5
145	Humber Bay	85	2355	2.2	196	St Clair R.	83	34	1.5
146	Canagagigue Ck	87	4	2.18	197	Oakville Harb.	85	2848	1.49
147	St Clair R.	83	17	2.18	198	Bluffers Park	84	2705	1.49
148	Rice Lake	87	13	2.17	199	Grand River	87	1	1.47
149	Collingwood H.	86	26	2.17	200	Hamilton (outer)		83	2097
150	Oakville Harb.	85	2842	2.17	201	St Clair R.	85	34	1.45
151	Bluffers Park	84	2706	2.16	202	St Clair R.	86	68	1.44

Table 4: cont'd.

Rank	Location	Year	Stn	SELScore
203	Penetang Harb.	85	525	1.42
204	Penetang Harb.	85	531	1.41
205	St Mary's R.	85	46	1.4
206	Bluffers Park	84	2703	1.4
207	St Clair R.	85	69	1.36
208	St Mary's R.	87	3	1.34
209	Rice Lake	87	15	1.32
210	St Clair R.	85	111	1.31
211	St Clair R.	86	203	1.31
212	Toronto Harb.	85	1379	1.3
213	St Clair R.	86	64	1.3
214	Canagagigue Ck	87	3	1.27
215	Collingwood H.	86	27	1.26
216	Collingwood H.	86	395	1.25
217	St Clair R.	86	110	1.22
218	Ashbridges Bay	84	2709	1.22
219	St Clair R.	86	38	1.22
220	Port Weller	85	2431	1.21
221	Bluffers Park	83	2084	1.21
222	St Clair R.	83	68	1.21
223	Collingwood H.	86	387	1.19
224	Rice Lake	87	4	1.19
225	East Headland	83	2038	1.18
226	East Headland	85	1391	1.18
227	St Clair R.	85	20	1.18
228	St Clair R.	86	219	1.18
229	Ashbridges Bay	84	2714	1.14
230	Niagara River	85	158	1.1
231	Ashbridges Bay	83	2036	1.07
232	Bluffers Park	83	2082	1.06
233	Ashbridges Bay	84	2708	1.03
234	Ashbridges Bay	84	2713	1.03
235	Toronto Main	87	10	1.02
236	Niagara River	83	126	1.02
237	Niagara River	83	148	1.02
238	Humber Bay	85	2339	1
239	St Clair R.	85	64	0.99
240	Collingwood H.	86	19	0.98
241	St Clair R.	84	102	0.97
242	Frenchman's Bay	83	2093	0.97
243	Bluffers Park	84	2701	0.94
244	St Clair R.	85	110	0.92
245	St Clair R.	83	64	0.92
246	Toronto Main	87	2	0.91
247	Ashbridges Bay	84	2710	0.9
248	St Lawrence R.	86	398	0.89
249	St Clair R.	86	115	0.87
250	Port Weller	85	2435	0.86
251	BluffersPark	84	2700	0.85
252	St Mary's R.	83	45	0.83
253	St Clair R.	85	68	0.83

Rank	Location	Year	Stn	SELScore
254	Rice Lake	87	5	0.83
255	St Clair R.	83	65	0.83
256	St Mary's R.	83	44	0.83
257	Collingwood H.	86	25	0.82
258	East Headland	83	2108	0.82
259	Collingwood H.	86	32	0.81
260	Niagara River	83	184	0.79
261	Collingwood H.	86	393	0.79
262	Ashbridges Bay	84	2716	0.79
263	Bluffers Park	83	2081	0.75
264	St Lawrence R.	83	359	0.73
265	St Mary's R.	85	44	0.72
266	Toronto Harb.	85	1367	0.7
267	Collingwood H.	86	28	0.69
268	Toronto Harb.	85	1352	0.69
269	St Clair R.	83	66	0.67
270	East Headland	85	2238	0.67
271	Bluffers Park	83	2085	0.67
272	St Lawrence R.	83	357	0.64
273	St Mary's R.	85	50	0.63
274	Toronto Harb.	85	1373	0.61
275	East Headland	85	2227	0.61
276	Penetang Harb.	85	526	0.59
277	Bay of Quinte	85	125	0.59
278	Penetang Harb.	85	527	0.59
279	St Mary's R.	85	78	0.57
280	Bay of Quinte	85	195	0.56
281	St Clair R.	85	66	0.56
282	St Lawrence R.	83	356	0.54
283	St Lawrence R.	83	360	0.53
284	St Clair R.	83	67	0.51
285	Humber Bay	85	2333	0.51
286	Toronto Main	87	4	0.49
287	East Headland	83	2102	0.49
288	Humber Bay	83	2339	0.47
289	Ashbridges Bay	84	2712	0.46
290	East Headland	85	2207	0.45
291	St Mary's R.	85	51	0.41
292	Toronto Harb.	85	1359	0.4
293	East Headland	83	2101	0.33
294	Bay of Quinte	85	192	0.3
295	East Headland	83	2103	0.3
296	St Lawrence R.	83	358	0.22
297	Bay of Quinte	85	181	0.11
298	St Mary's R.	83	51	0.06
299	St Mary's R.	83	50	0.05
300	Bay of Quinte	85	156	-0.48
301	Bay of Quinte	85	346	-0.97
302	Bay of Quinte	85	161	-1.05
303	Bay of Quinte	85	199	-1.07
304	East Headland	85	2200	-6.01

Figure 2

In-place Pollutants Program

Windermere Basin and Hamilton Harbour PSQG severe effect level (S.E.L.) metal guideline exceedances

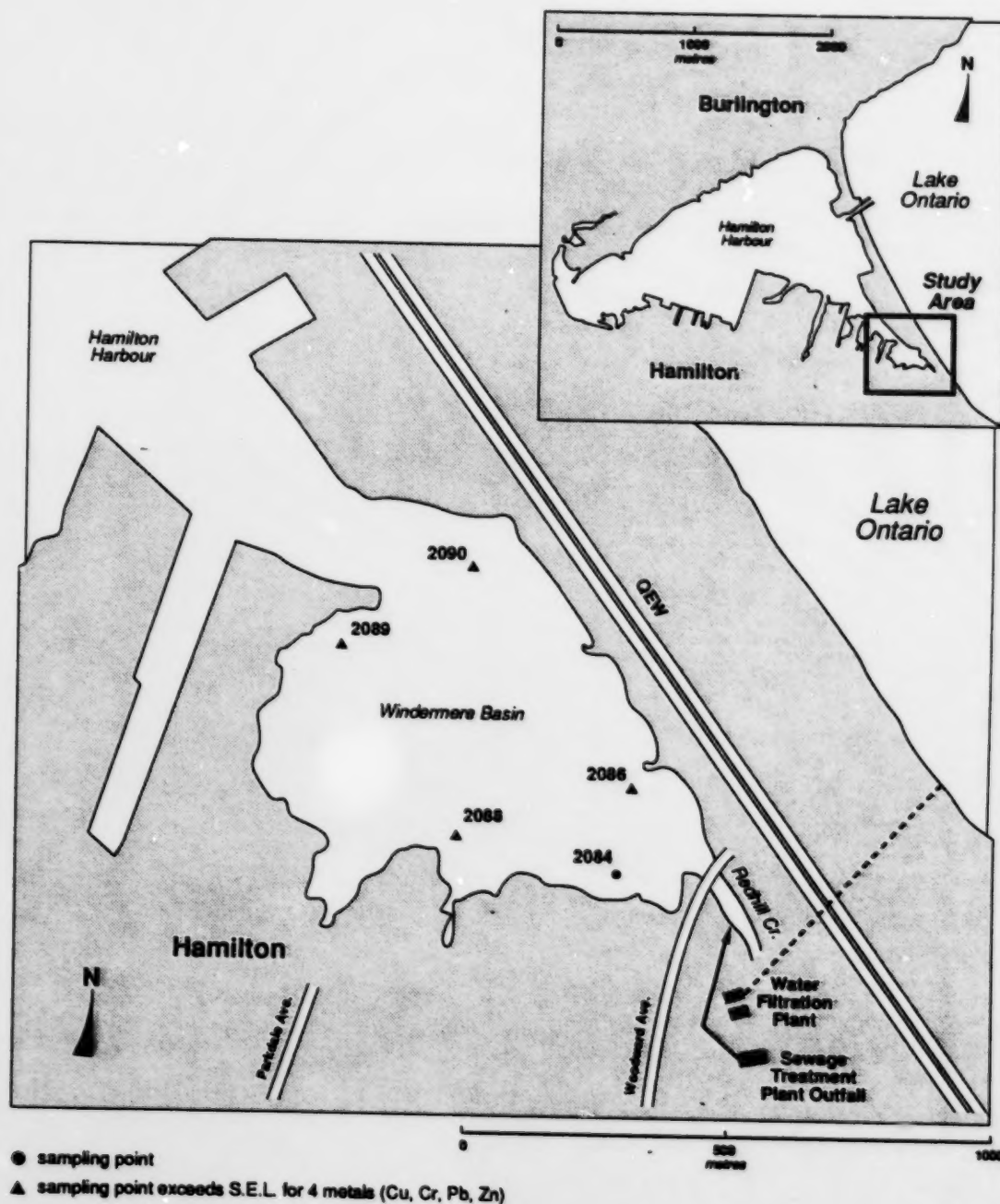


Figure 3

In-place Pollutants Program

Toronto Waterfront and Humber Bay PSQG severe effect level (S.E.L.) metal guideline exceedances

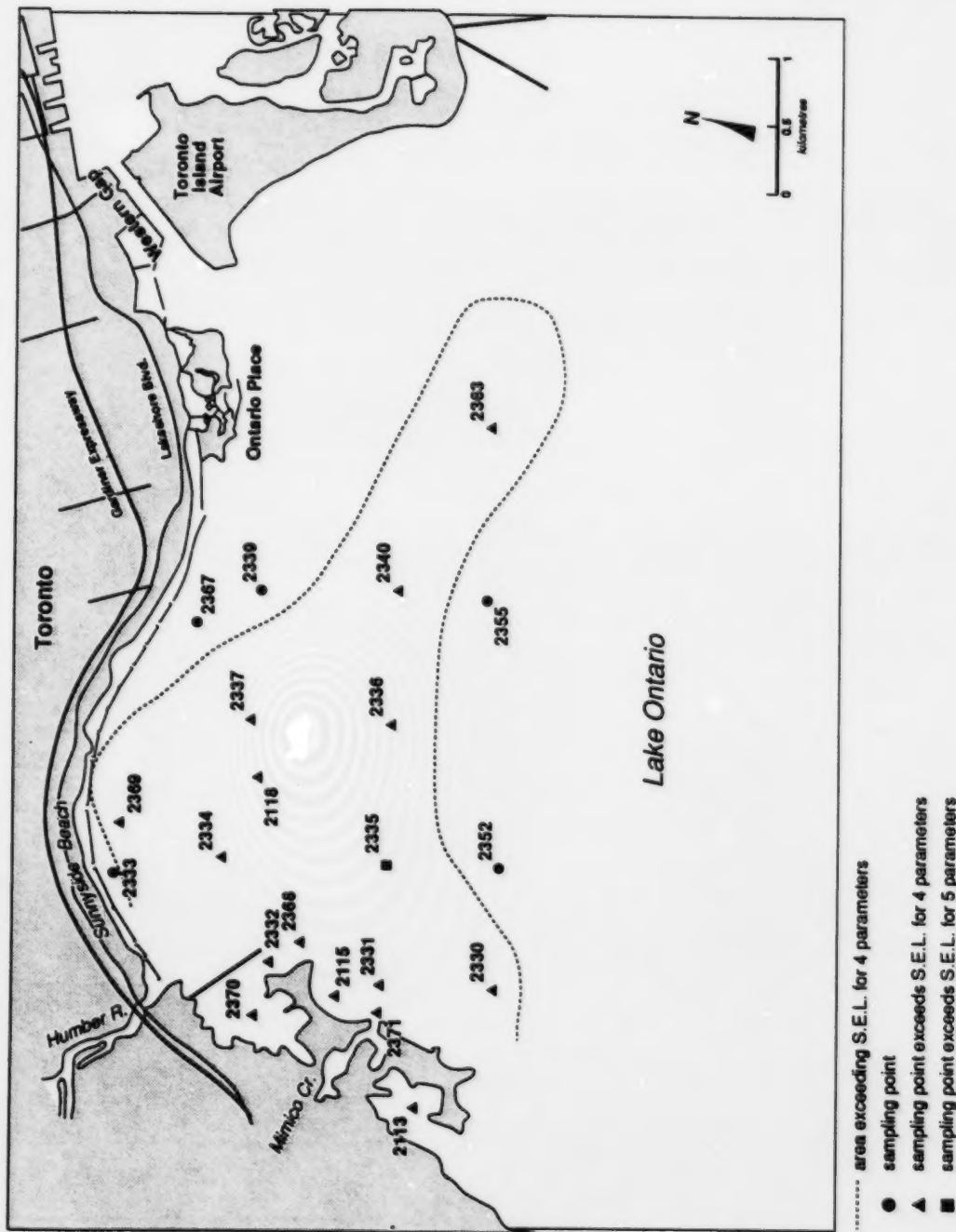


Figure 5

In-place Pollutants Program

***Detroit River PSQG severe effects level (S.E.L.)
metal guideline exceedances***

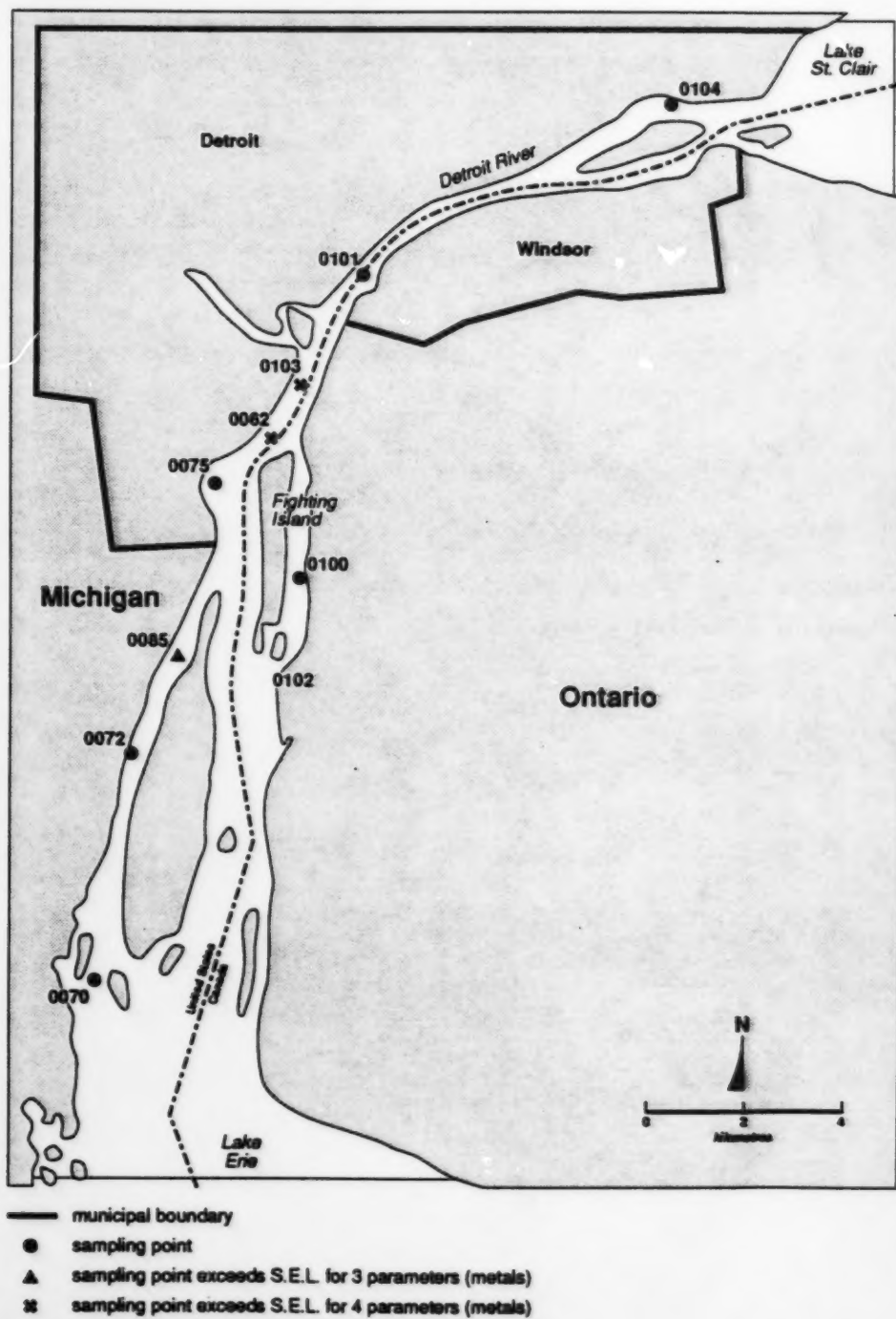
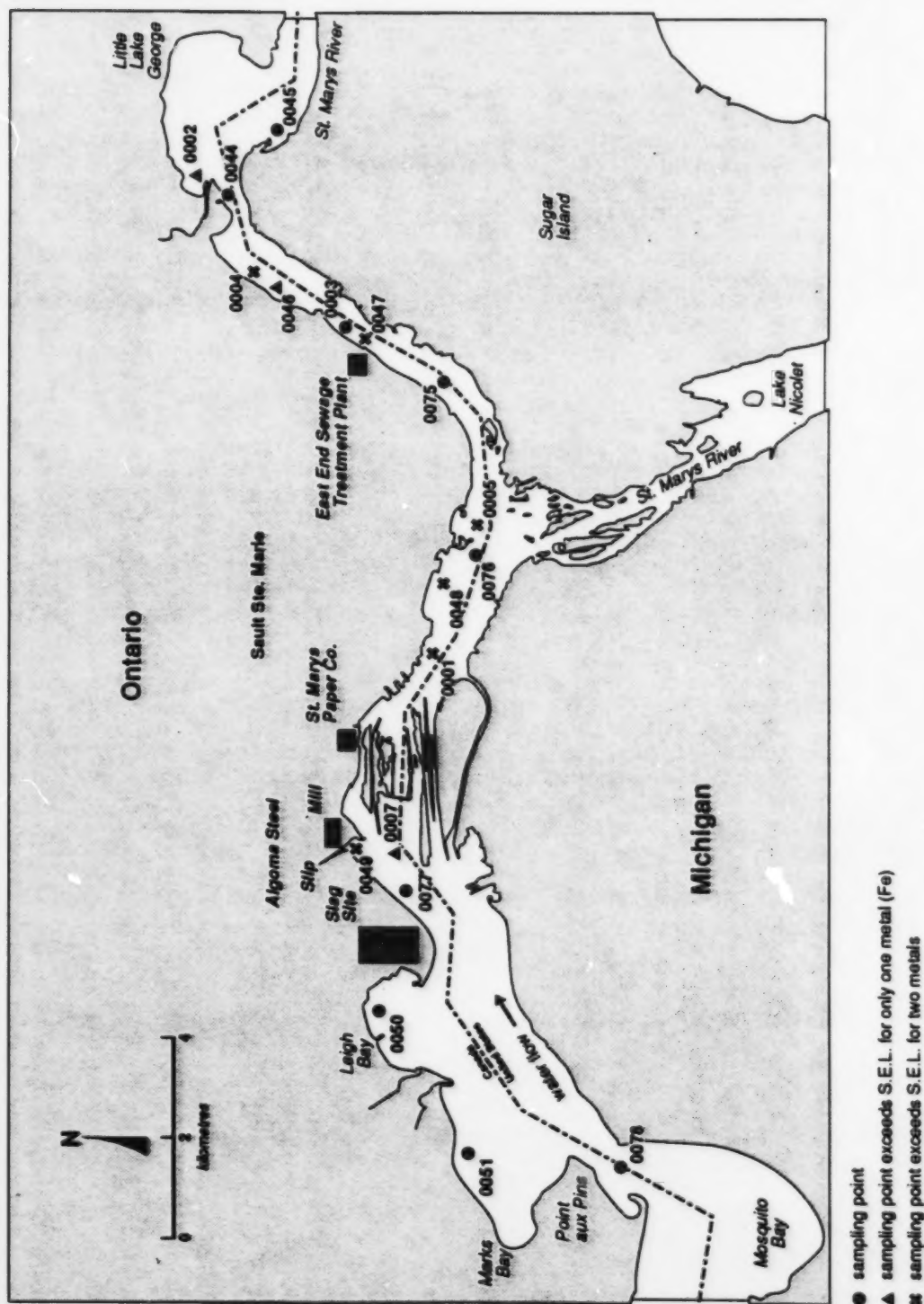


Figure 6

In-place Pollutants Program

St. Mary's River PSQG severe effect level (S.E.L.) metal guideline exceedances



concentrations of metals in sediment at some sites, for many metals, over 50% of the sites sampled fell below the Lowest Effect Level of the proposed Provincial Sediment Quality Guidelines and can be considered as clean. This is a significant finding, since the choice of study locations was originally based on known or suspected contamination in these areas. These results indicate that the problem of severe contamination is localized to a few areas. However, the results also show that large areas are contaminated above the Lowest Effect Level, and could potentially effect benthic organisms in these sediments. Since the sources of these chemicals have not, for the most part, been controlled it is apparent that contaminants can and will continue to accumulate at these locations. These areas are of potentially greater concern, since it is an easier task to prevent their degradation to the Severe Effect Level, than it is to remediate them once this has occurred.

At those locations where sediments exceeded the Severe Effect Level(s), zones or gradients of contamination exist and not all areas within the Toronto Harbour or Humber Bay, for example, are heavily contaminated. However, the zones of low sediment contamination generally appear to coincide with low levels of sediment organic matter. The sandy areas of Humber Bay, as just one example, were generally well below the guidelines for all metals, while areas of silty sediments generally had much higher contaminant concentrations, frequently exceeding the Lowest Effect Level guidelines and in some cases the Severe Effect Level guidelines as well (Figure 3). Toronto Harbour and Ashbridges Bay have similar zones of greatest impact (Figure 4). In Toronto Harbour, the areas of high silt/clay content were areas of higher metal accumulation, while the sandy sediments near the Toronto Islands were much lower.

In nearly all of the cases where concentrations exceeded the Severe Effect Level guidelines, the sources can be traced back to a few point source discharges. Non-point sources do not appear to be major contributors to the sediment contaminant load in these areas, though in many cases they are important additional sources. Extreme levels of metal accumulation are most readily associated with specific sources of discharge in many of the study locations. Non-point sources appear to be major contributors to sediment contaminant levels in those areas where concentrations fell between the Lowest Effect Levels and the Severe Effect Levels. Both point to the need for source control and strongly suggest that source control would likely be the single largest factor affecting sediment quality. Certainly, no remedial action

regarding sediments should be undertaken before source control has been achieved. Any remedial action that is undertaken should be carefully evaluated in light of the sediments themselves, particularly in relation to potential for release if the sediment is disturbed.

The tendency of metals to bind with organic matter was not consistently reflected in the results. The analysis of the entire In-Place Pollutants data set yielded no significant statistical correlation between sediment metal concentrations and sediment TOC on a province-wide basis, though strong significant correlations were obtained between the various metals. These correlations simply suggest that a number of the metals are deposited in sediments together. Generally, the sources for metals (storm sewers, municipal sewers, industrial outflows and even natural weathering of rock) also discharge other types of contaminants including organic material. The association of metals with particles could therefore be either at the source, or could be the result of binding with particles in the water column or at the sediment surface.

Despite the overall lack of a relationship between metals and organic matter (TOC), at many of the individual study sites sediment metal concentrations were highly correlated with TOC. Metal accumulation in the St Mary's River was strongly and significantly correlated with sediment TOC in 1985 (Jaagumagi *et al.* 1991b). Similarly, sediment metals correlated strongly with sediment TOC at the Toronto Main STP (Jaagumagi *et al.* 1991a). Conversely, no correlation was obtained between sediment metals and sediment TOC at Rice Lake and Grand River study sites, and only sediment Ni and TOC were correlated at the Canagagigue Creek study site (Jaagumagi *et al.* 1989a, 1989b, 1989c). However, the lack of a significant correlation between sediment TOC and sediment metal concentrations may merely indicate that the contaminant is associated with a specific source of discharge and thus confined to a local area.

While significant correlations were found between metals and TOC at some of the sites, no predictable relationship between sediment TOC and metal concentrations could be developed using the In-Place Pollutants data set. The areas highest in organic matter did not necessarily have the highest sediment metal concentrations and in some cases metals were found to accumulate to high concentrations in sediments that were low in TOC. This suggests that other sediment fractions are also serving as reservoirs for metals and that metal

accumulation is more a reflection of local discharges than the presence of organic matter. It appears that accumulation in sediments can be facilitated by organic matter but that it is not limited by it. The presence of organic matter in an area receiving heavy metal discharges merely provides one sediment phase in which metals may accumulate.

For example, Appendix Table 1a shows that Rice Lake TOC concentrations at 180 mg/g, and second, Bay of Quinte TOC concentrations at 140 mg/g, were the highest of any of the In-Place Pollutants locations. Yet, Rice Lake ranked as relatively clean in terms of metal concentrations (Table 1a, Appendix) while Bay of Quinte sediments were moderately contaminated. The areas of moderately high TOC concentrations, such as the Toronto Waterfront and the Windermere Basin (Hamilton Harbour), had the highest contaminant concentrations (Table 1a, Appendix). In some cases, such as the Toronto waterfront, this is likely due to the organic enrichment of these previously mesotrophic areas as a result of anthropogenic influences and the co-accumulation of contaminants with the organic matter. In contrast, those areas naturally high in organic matter, such as Rice Lake, have been exposed to less anthropogenic influence (such as industrial or municipal discharges), since these areas have generally not been highly populated or developed. Therefore, the degradation of sediment quality appears to have occurred primarily in areas of previously mesotrophic conditions, and degradation appears to have occurred as a combination of organic enrichment and associated contaminants.

While metals in aquatic environments generally bind to particles, these particles can be composed of a number of components (Luoma 1985). The sediment components that are capable of most strongly binding metals, such as organic particles and the Fe/Mn oxides, usually occur as coatings, often covering clay surfaces. Clays by themselves have been found to be much less important than other types of sediment components in binding metals in sediments, due to a combination of lower binding intensity and a loss of binding sites to other components (Luoma 1985).

The distribution of a metal among the sediment components is determined by: 1) the intensity of metal binding to each component; 2) the number of available binding sites per unit mass of each component; and 3) the mass of each component per unit mass of sediment (Luoma 1985).

Luoma (1985) noted that no single sediment

component dominates the partitioning of a metal; and that partitioning may change as sediment conditions change.

The discussion that follows explores some of the mechanistic explanations of how metals are incorporated into the various fractions of sediments.

1.3 Metals in Sediment Geochemical Fractions

1.3.1 Theoretical Considerations

Metals will often bind preferentially to different components of the sediment. Various extraction schemes have been devised to determine the geochemical fractions in which the metals occur, or alternatively, the potentially available metal in a sediment. Most such extraction schemes are operationally defined (i.e. the amount released during a given extraction step will be a reflection of what can be desorbed by the chemical used, rather than the amount actually in the given geochemical phase) and thus may not reflect the actual distribution of the metal in sediment. A sequential extraction scheme was used in the In-Place Pollutants Program. This is an operationally defined process that separates the various components in the fine-particle (<63 μ) fraction. The concentration of metals can be measured in each of the following geochemical phases:

- IW - Interstitial Water
- F1 - Cation Exchangeable Fraction
- F2 - Easily Reducible or Carbonate Bound
- F3 - Organic Complex
- F4 - Fe/Mn Oxide Fraction
- Res- Residual Fraction

The details of the extraction procedure and the significance of each fraction are discussed in Per-saud *et al.* (1987) and Tessier (1979).

Metals in sediment can undergo changes in binding to different sediment fractions during ageing (diagenesis) of the sediment, with movement generally being towards the more resistant fractions (e.g. Andrews 1988). The movement and change in binding that metals undergo over time has significant implications for aquatic organisms. Over time, a general reduction in availability from aged sediments could be expected, and thus this is just one more in a complex array of factors affecting contaminant release/availability. Changes in availability through diagenesis also have implications for using

spiked sediments in laboratory tests for toxicity or bioavailability and suggest that the application of laboratory results to field conditions will be extremely complex.

The process of diagenesis can also provide useful clues in sediment assessment studies. The relative amounts held in the more easily extractable fractions as compared to the residual fraction may serve to identify metals in sediments that are of recent origin and those that are historical or aged deposits.

The importance of metal binding to the various sediment fractions is that potential for release of the metal varies among the fractions. Metals bound to the more resistant fractions are generally tightly held and thus not usually available for release. The metals held in the less strongly bound fractions can, under certain circumstances, be released back to the water column or the pore water. Thus, the availability of metals both to organisms and for release to the water column, is strongly influenced by their distribution within the various fractions.

The sequential extraction procedure used to determine the distribution of metals in sediments separates the sediment-bound metal into six operationally defined phases, based on a range (weak to strong) of chemical extractants. The basis of the extraction scheme is the assumption that the operationally defined phases are more or less representative of the natural distribution of metals in sediments. This however, has not been proven and a number of problems have been identified with the various extraction procedures in use.

Metals in the interstitial water or porewater do not necessarily relate to concentrations in the sediment solid phases. Forstner (1990) notes that while adsorption/desorption processes seem to control concentrations of As and Cr in anoxic porewaters and thus concentrations of these metals would depend on the sediment solid phase concentrations, some metals (e.g. Cu, Zn and Cd) in sulfidic porewaters are controlled mainly by precipitation/dissolution processes and under these conditions are independent of the concentrations in the sediment solid phases.

In the approach used by MOE, the major sediment solid phases are divided into the adsorbed fraction (F1), metals bound to carbonates (F2), those bound to organic matter and sulphides (F3), those sorbed to iron/manganese hydroxides (F4) and those in the residual phase (F5). In addition to

the solid fractions, metals in sediments can exist in the dissolved phase, namely the porewater.

Metal association in the adsorbed phase (F1) is usually through cation exchange on the sediment surface and this fraction is often referred to as the cation exchangeable fraction. The adsorption of metals to this phase depends on the cations present and the surface type. This is generally the most reactive phase, and metals can be readily adsorbed or released from this fraction, depending on the relative binding intensities of the cations present.

Carbonates occur in sediments mainly as polymorphs of calcium carbonate. The most common association of metals with carbonates (F2 fraction) is through substitution reactions with calcium or magnesium either on the mineral surface or in the lattice structure (Campbell *et al.* 1988). Forstner and Wittmann (1981) suggest that coprecipitation with carbonate (i.e. sorption onto the surface and subsequent incorporation into the crystal lattice) may be important for only certain metals, such as cadmium, lead and zinc, and only where carbonates form a major component of the sediment. In general, carbonates tend to be relatively insoluble. Campbell *et al.* (1988) noted that the concentrations of metals in carbonates is relatively minor, compared to the other sediment fractions, though again, coprecipitation with carbonates can be of significance in alkaline waters.

Metals appear to have a particularly high affinity for organic particles. Organic particles in sediment can consist of a variety of mixtures of animal and plant detritus in various stages of decomposition, that range from colloids to large fragments (Campbell *et al.* 1988). Organic matter can also occur as coatings or adsorbed on other substrates. Together with the iron/manganese hydroxides, organic particles form the major binding fractions for metals in sediments. The organic fraction appears to assume the greatest significance in those sediments where the relative levels of iron/manganese hydroxides are low. Thus, Campbell *et al.* (1988) noted that in the depositional zones of lakes, where organic matter accumulates, the metals were associated with organic matter, while in the erosional areas where organic matter was low, the iron/manganese hydroxide fraction was the largest repository.

Operationally, it is difficult to separate the organic and sulphide bound fraction in the extraction procedure used by MOE and the results are reported together (i.e. the F3 fraction). The sul-

phide-bound metal assumes greatest importance in anoxic sediments, where, in the presence of sulphide minerals such as ferric sulphide (FeS) metal sulphides can be formed upon the dissolution of Fe hydroxides and release of Fe. The decay of organic matter can also result in the release of metals from this matrix and the subsequent formation of metal sulphides. Recent studies by Di Toro *et al.* (1990) suggest that the sulphide fraction in some sediments may be the controlling factor in the toxicity and bioavailability of certain metals such as cadmium.

The Fe/Mn hydroxides in the water column, along with organic particles, are significant scavengers of other metals. The metals can be coprecipitated with the hydroxides, or they can adsorb to the surface of the sediment. Hydroxide formation is a process associated with oxic conditions in the water column and the sediments. Under anoxic conditions, the hydroxides dissolve, releasing iron, manganese and any scavenged metals. These are free to read-adsorb to other components in the sediment, and under anoxic conditions will often form metal sulphides.

The four phases described above are generally the more available in terms of potential release to the water column or availability to organisms, though it is recognized that a gradient of availability exists. A number of these phases, such as the sulphide bound and the hydroxide bound, serve as effective sinks for metals, though under certain circumstances, even these can result in release of metals from the sediment. Metals in the other two phases, the cation exchangeable (F1) and the easily reducible (F2) are potentially more available, though the concentrations of metals in these two phases is generally lower than the other phases.

The residual phase, by comparison, is the primary sink for metals. These are the metals held within the lattice structure of minerals (commonly silicates) and the metals held in this fraction are usually considered to be unavailable. Campbell *et al.* (1988) attribute metals in the residual phase to terrigenous (allochthonous) sources, and to weathering and diagenesis. Evans (1988), and Andrews (1988), in laboratory tests with contaminated sediments found an increase in metal content in the residual fraction over time and attributed this to movement of the metals into the most resistant phases as the sediment aged.

Much of the metal loading to water bodies, especially from anthropogenic sources, enters the sediments bound to the organic fraction, and second-

arily to the Fe/Mn hydroxides fraction. Analysis of the relative concentrations in each, as compared to the residual fraction, can provide some clues as to the origin and residence time in the sediments. It can also provide an indication of metals that may be originating from natural sources in a watershed, versus those of anthropogenic origin.

In practice, most extraction procedures provide, at best, an estimate of the relative distribution of metals in various geochemical phases of sediment. The concentrations of a metal in each phase cannot be regarded as absolute, since there appears to be some redistribution of metals among the phases during the extraction procedure (Hart and Andrews 1991).

Recent information also suggests that some of the earlier theories regarding the reduction in availability of metals in some of the more resistant fractions under natural conditions may no longer be applicable. Francis and Dodge (1990), as just one example, found that microbial action could result in significant remobilization of toxic metals coprecipitated with iron oxides.

1.3.2 Program Synthesis

The major objective of the use of the sequential extraction of metals by MOE was to determine whether any relationship could be established between the levels in the various phases and levels in the tissues of organisms that inhabit the sediments. These results are explored in section 4.

In addition to the use of sediment geochemical fractions in determining the potential availability of metals in sediment to biota, metals in the various geochemical fractions can provide some insight into the origin of metals in sediment. The amount of metal in a specific geochemical fraction can give some indication of the source (e.g., natural vs. anthropogenic) and age (i.e. recent or historic) of the metal in the sediment. Andrews (1988) and Evans *et al.* (1988) found that the amount of metal in a specific geochemical fraction could change over time (through diagenesis), with movement generally towards the more resistant fraction. The relative amount held in the F3 fraction, over the amount in the sum of all sediment fractions was used in specific sites to assess the relative age (time of origin) of the metals in the sediment. However, since the F3 fraction also contains the metals held as metal sulphides, this is not necessarily accurate

and may merely reflect the changes in redox condition and the subsequent formation of sulphides.

The comparisons worked best on a site-specific basis. At a number of locations where sources are still active it was found that the concentration of metals in the F3 fraction was higher than in areas removed from the source. For example, in Rice Lake, the concentrations of all metals increased in the F3 fraction at stations in Peterborough. Similarly, in the St Mary's River, concentrations in the F3 fractions close to the Algoma Steel mill were higher than either upstream or downstream. Thus, the amounts held in the various geochemical fractions can indicate not only the potentially available metal, but can also suggest whether the sediment concentrations are of recent origin.

Data on individual sites have not been provided in this report. However, all geochemical results are available for the In-Place Pollutants Program in Persaud *et al.* (1989) and Jaagumagi *et al.* (1989a, 1989b, 1989c, 1991a, 1991b).

The use of geochemical fractionation in delineating the routes of uptake of metals by aquatic organisms has met with only limited success (see Section 4). Perhaps with further refinement, the use of geochemical fractionation data may provide useful information in relation to the bioavailability of a metal. Currently, there is little to be gained in evaluating the geochemical distribution of metals in sediments with regard to management decisions. However, based on recent advances in understanding the mechanics of metals uptake by organisms from sediment, metal geochemistry may become a potentially significant factor in assessing the effects of metals contamination of sediments.

1.4 Contaminants in Sediments - Organic Compounds

1.4.1 Theoretical Considerations

Organic compounds can be classified into two basic types - ionic and nonionic (also called polar and nonpolar respectively) - which are characterized by their different behaviour in water. Ionic compounds behave similarly to the metals by dissociating into an anion and a cation. Most dissolve in water and sorption in ionic compounds is mainly redox (Eh) and pH dependent (e.g., PCP in a pH range of 6-7 is predominantly in the completely ionized form (Fry and Fisher 1990)). The majority

of these compounds are not persistent and thus are generally not found in sediments. However, persistence can vary among compounds, depending on the number of chlorine atoms, with some of the more chlorinated compounds persisting in sediments. Persistence can also be due to the neutral forms of a compound, which adsorb to a greater degree and thus behave similarly to the nonionic compounds (Jahvert 1990). Some compounds, such as chlorophenols, appear to form complexes with some of the sediment constituents such as the iron and manganese hydroxides.

The nonionic compounds do not dissociate into ions but, rather, partition (i.e. sorb directly without any dissociation of the compound) to other components such as dissolved organic matter and particulate organic matter. Most of these compounds are highly hydrophobic and the nonpolar organic compounds therefore have a high affinity for organic matter in both the water and the sediments.

The tendency of an organic molecule to partition to organic matter, relative to its tendency to partition to water, can be expressed as a ratio. Partition coefficients, as these ratios are known, usually measure the amount of a compound partitioning to an organic solvent, commonly n-octanol, relative to the amount partitioning to water (i.e. free-floating, in an undissociated state). These are expressed as K_{ow} . For hydrophobic compounds, the log of the ratio is usually above 4, indicating that the compound is at least 10,000 times more soluble in an organic solvent than in water. Since lipids are similar to organic solvents, the partitioning behaviour of a compound is significant in terms of its bioaccumulation potential. Those that exhibit strong partitioning to organic matter would also be expected to show a strong affinity for lipids, with the result that these would be expected to accumulate in organism fat tissues. Bioaccumulation of these compounds, then, comes to depend in part on the efficiency of the sediments as a sink as compared to the efficiency of organism lipids. The partitioning behaviour of a compound is also significant in terms of its potential for accumulation in sediments and for its potential release from the sediments either to organisms or to the water. Evidently, the more hydrophobic compounds would partition rapidly to sediment, and would also be expected to adhere strongly to them.

The theoretical partitioning behaviour of organic compounds is not always observed in the field. Readman *et al.* (1987) (in Galassi *et al.* 1990) showed that the actual concentrations of polycyclic

aromatic hydrocarbons (PAH) in water could be up to 2.5 orders of magnitude lower than predicted by equilibrium partitioning theory. Landrum and Robbins (1990) note that clays may also contribute to sorption of organic compounds and thus reduce availability to below predicted levels. They go on to note that sorption is also strongly influenced by particle size as well as organic matter.

Smith *et al.* (1988) and Knezovich *et al.* (1987) noted that hydrophobic organic compounds have a high affinity for organic matter, and will partition rapidly to sediments, suspended particles, and to a lesser degree, dissolved organic matter. In contrast, ionic compounds dissociate into ions and are transformed usually through photolysis, hydrolysis or biodegradation. While the nonpolar organics can also undergo these transformations, the reactions are generally much slower due to the stability of these compounds.

While nonionic compounds generally persist for long periods of time in the sediments due to their chemical stability, there is growing evidence for at least some biodegradation of these compounds.

Brown *et al.* (1987) found that PCBs underwent reductive dechlorination in aerobic sediments, and the products themselves were also oxidatively biodegradable by bacteria.

Chen *et al.* (1988) observed that in laboratory cultures, PCBs in anaerobic sediments can undergo biodegradation, though the more highly chlorinated PCBs appear to be more resistant. Nies and Vogel (1990) found that organic solvents used to introduce PCBs into laboratory tests of dechlorination aided significantly in the rate of dechlorination. They concluded that while some dechlorination was likely to occur in *in situ* sediments, the process was likely to be very slow. Larsson and Lemkemeier (1989) found that the presence of humic matter aided in the microbial mineralization of chlorinated aromatics and concluded that the more rapid rate was due to the presence of microbes in humic-rich water that are capable of cleaving phenolic rings.

Hagblom and Young (1990) noted that chlorophenols were degraded under sulphate reducing conditions and degradation was coupled with sulphate reduction.

The input of persistent organic contaminants to the sediments from allochthonous sources in a watershed is generally dependent on the nature of the compound and the presence of complexing

agents. For the nonpolar compounds, the presence of organic matter in the water column is a significant factor in determining the concentration of contaminant in the sediments. While studies have shown that even for the highly insoluble compounds, the freely dissolved form predominates in the water column (Eadie *et al.* 1990; Eisenreich *et al.* 1988), partitioning to suspended matter and subsequent settling to the bottom can contribute significant quantities to the sediments. In addition to the chemical solubility of a compound, other factors such as particle size and concentration, settling velocity, and sorting and resuspension all determine the areal extent of contamination of bottom sediments.

Gilliom and Clifton (1990), in studying the extent of contamination in the San Joaquin River system, found that the concentration of DDT (including DDD and DDE) in suspended sediment was 3-4 times higher than concentrations in the bed sediments. They concluded that erosion of sedimentary materials from upstream sources (land based sources as well as bed sediments in smaller tributaries) were contributing high concentrations of contaminated sediments to downstream areas. This study found that over 50% of the total DDT in the water column was carried by the suspended sediment. Much of this originates as sediment-bound material resuspended from upstream areas of the drainage basin and differs from areas where direct input of the contaminant may result in the freely dissolved form predominating in the water column.

Lau *et al.* (1989) also found that suspended sediment accounted for most of the downstream transport of contaminants in the St. Clair and Detroit River. The high proportion carried in the suspended sediments was felt to be at least partly due to the discharge of most of the contaminants in particulate form.

Thus, it seems that the suspended sediment concentration of the receiving water and the form in which the compound is discharged both influence the extent of the area that is affected by the contaminant.

Ferguson and Metcalfe (1989) found that the resuspension and transport of contaminated sediment could be a significant factor in the movement of contaminants over a broad area. Sediment in Little Lake in the Otonabee River was believed to be the principal source of PCBs found further downstream and was responsible for PCB contamination in a broad area of the waterway. The

affinity of organic compounds, such as PCBs, for organic matter means that resuspension and transport of contaminated sediments is a major concern with regard to the spread of contaminated sediments.

Lum *et al.* (1987), in calculating a sediment budget for Lake Ontario for Mirex, estimated that 94% of the suspended sediment entering the lake is retained in the depositional basins of the lake. Therefore, by inference, it would be expected that all contaminants that associate predominantly with the particulate phase, would also be retained.

In most waterbodies, considerable sorting and movement of sediment occurs, which can redistribute contaminants over broad areas, or can result in the accumulation of contaminated sediments in depositional areas. Oliver *et al.* (1989) noted that sediment deposition and resuspension resulted in the deposition of fine grained material, together with its contaminant load, in the deeper basins of Lake Ontario. The result was accumulation of contaminated sediments in the deep basins, and less accumulation of contaminated sediments in the shallow, erosional areas.

A second major group of insoluble organic compounds that are persistent in sediments is the polycyclic aromatic hydrocarbons (PAHs). In many respects these appear to behave like the organochlorine compounds, but with some differences. The complex ring structures of the higher molecular weight compounds generally makes these compounds even more insoluble than the organochlorines. Partition coefficients range from $\text{Log } K_{ow} = 3.37$ for naphthalene to $\text{Log } K_{ow} = 7.66$ for indeno[1,2,3-cd]pyrene (CCREM 1987).

Unlike the organochlorine compounds, which originate from anthropogenic sources, many of the PAH occur naturally, principally through combustion processes. Therefore, natural background concentrations of these compounds exist and so, presumably, do biological mechanisms for coping with these at natural levels. Many are typically associated with a specific origin and thus may serve to identify the source of the compound.

Umlauf and Bierl (1987) found that within the suspended sediment itself, organic compounds demonstrated an affinity for different size fractions. In that study, the silt and clay fraction, which represented only 8.1% of the total sediment material, was found to carry 60-70% of the contaminant

(in this case, PAHs) load. Since this is the size fraction most easily remobilized, this represents a significant amount of contaminant that can re-enter the water column or be available to water column organisms. Fractionation of the suspended sediment size fractions revealed that 60% of the total PAH load was carried by the middle (6.3-20 μm) silt fraction. However, the authors concluded that the extent of adsorption depended not only on the physico-chemical properties of the contaminant and organic carbon content of the sediment, but also on the chemical properties of the organic matter in the different particle size fractions. In general, the high molecular weight PAHs were strongly associated with sediment. The low molecular weight compounds were more often present in the water column in the freely dissolved form.

For PAHs, biotransformation can play a significant role in their fate in aquatic systems. Though generally lacking in most invertebrates (some invertebrates have been found to be capable of metabolizing these compounds, though most of these organisms appear to be marine (e.g., Lee 1986)), many higher organisms possess enzymes for metabolizing PAHs. A number of these metabolic products have been identified as carcinogens. Microbial activity in the sediments has also been shown to be capable of metabolizing PAHs. Gibson (1977) found that some sediment microorganisms possessed the ability to oxidize certain PAHs to metabolic products similar to those that are formed by mammals.

McElroy *et al.* (1987) found that more than 80% of the benz[a]anthracene added to mesocosms was degraded, but that polar degradation products persisted for over 200 days, suggesting that degradation products may be a significant portion of the total PAH in sediments. The sediment-water interface was identified as the major site of microbial mineralization. In further studies, McElroy *et al.* (1990) concluded that benz[a]anthracene from the water column was more available for microbial mineralization to CO_2 (as well as uptake by biota) than the entire sediment reservoir, suggesting that, in sediments, PAHs have the potential to persist for extended periods.

In addition to resuspension of sediment, bioturbation can also play a significant role in the remobilization of contaminants. Bioturbation can affect contaminant movement from sediment by increasing penetration of oxygenated water into the reducing zone, thus changing the position of the redox boundary. Bioturbation can also result in the physical

transport of sediment from the deeper layers to the sediment surface (Santschi *et al.* 1990). Karickhoff and Morris (1985) found that in laboratory experiments, tubificid oligochaetes could transport over 90% of the chemicals HCB, pentachlorobenzene and trifluralin from the biologically worked zone within the sediment to the sediment surface in 30-50 days. Subsequent release back to the water column depends on the characteristics of the compound. For those investigated, they found that less than 20% of the compound contained in the faeces was actually released.

Fisher *et al.* (1980) (in Santschi *et al.* 1990) concluded that the upper 6-9 cm of the surface sediment of Lake Erie was passing through the guts of tubificid worms 14 times per year. Fisher *et al.* (1980) also concluded that in Lake Michigan, the biologically mixed layer, which is in the order of two to four cm, represents 20 to 40 years of accumulated input.

McElroy *et al.* (1989) noted that bioturbation significantly affected PAH distribution in sediment, increasing the flux of these compounds to the water column.

1.4.2 Program Synthesis

The assessment of sediment contamination by organic compounds sought to address two concerns. First, the study sought to determine the extent of sediment contamination at various sites where sediments were known or suspected of being contaminated by organic compounds. The second aim was to determine whether sediments, which have in the past been regarded as merely sinks for contaminants, could also act as a source to the water column and/or to aquatic biota. Biological effects from contaminants in sediments could be manifest in two ways: they could contribute to biota tissue levels and they could act at the population or community level, resulting in changes in community structure in those areas where sediment contamination was high.

Organic contaminants were generally not present at detectable levels in sediment in most of the areas studied. Exceptions were DDT and its metabolites, the PCB group and the PAHs. These compounds were found to occur, either singly or in combination, at a number of the study locations. The most significant were the Detroit River, Canagagigue Creek, St Mary's River, Toronto Waterfront, the St Clair River, the Rice Lake-Otonabee

River system and the St Lawrence River (Appendix Table 2 and Table 3).

The distribution pattern of organic compounds strongly suggests that their presence was due to specific sources of input. In those areas where these compounds were present above detection limits, they occurred at high concentrations and the distribution was often localized around the source. Most areas of high sediment organic contaminant concentration were areas of high sediment organic matter accumulation. It is not surprising that the hydrophobic compounds accumulated in these areas, considering the affinity of these compounds for organic carbon. Potentially, these areas can also serve as sources of contaminant dispersal through resuspension and biological accumulation.

Appendix Table 2 lists the PCB and pesticide concentrations in sediment at the IPP study sites. Overall, of the 17 organic compounds for which guidelines have been proposed (Persaud *et al.* 1990) the Severe Effect Level was exceeded for three compounds. In total, only four exceedances of the PSQG were noted and these were for ppDDD (two stations) and ppDDT in Canagagigue Creek, and HCB at one station in the St Clair River. No exceedances of the Severe Effect Level by any of the other parameters was noted at any of the stations, though in many locations the Lowest Effect Level was exceeded for a number of compounds. Exceedances of the proposed Provincial Sediment Quality Guidelines are summarized in Table 5.

While the program was able to show that contaminants are accumulating in sediments as a result of specific sources of discharge, it is also noteworthy that in a large number of areas the sediment concentrations were below the detection limits. The distribution of the organic compounds was not as pervasive as the distribution of metals. Where high concentrations did occur, these were generally localized, though in some cases, particularly flowing water situations such as Rice Lake or the Niagara River, contaminants did appear to be migrating downstream or away from the source.

Concentrations were below detection limits in the majority of locations sampled. Clearly, the most pervasive of these compounds was the PCBs, which were found above detection levels at over 50% of the sites. The results also suggest that non-point source inputs, such as atmospheric transport and agricultural runoff, are not contributing to sediment contaminant problems on a wide scale to a sig-

Table 5: Percentage of Stations Exceeding the Provincial Sediment Quality Guidelines.

CHEMICAL	Above L.E.L.	Above S.E.L.
HCB	4	0.3
Heptachlor epoxide	8	0
Aldrin	0	0
Mirex	3	0
α -BHC	1	0
γ -BHC	2	0
β -BHC	1	0
α -Chlordane	7	0
γ -Chlordane	5	0
PCBs	36	0
ppDDE	19	0
ppDDD	14	0.3
ppDDT	6	0.3
opDDT	1	0
Dieldrin	23	0
Endrin	12	0

nificant degree. However, there are indications that these can contribute to local problems of contamination.

Sediment sampling for PAHs was not begun until 1985, for which some data were available. Unfortunately, areas that could potentially be high in sediment accumulated PAH, such as Hamilton Harbour, were not sampled, and comparison of areas on the basis of PAH contamination is limited.

Of the areas sampled, the highest concentrations were in the Toronto Waterfront at Ashbridges Bay and the East Headland lakefill, the St Mary's River, Rice Lake in the Otonabee River at Peterborough and the St Lawrence R. at Cornwall (Appendix, Table 3). In all of these cases, sediment accumulation is associated with specific sources and these represent the three major anthropogenic sources of PAHs to sediment; urban runoff, coal tar wastes from coal gasification, and coking plant wastes. Though the levels were highest at these locations, some stations in Collingwood Harbour, the Grand River and Canagagigue Creek also exceeded the lowest effect level guidelines for total PAH. None of the locations sampled exceeded the Severe Effect Level.

Sediment concentrations of chlorophenols were generally below detection limits. Two areas, the Kam River in Thunder Bay and the St. Lawrence River at Cornwall, were the only locations at which detectable concentrations were found (Appendix, Table 4). Chlorophenols are usually associated with specific sources (industrial processes) and their distribution would not be expected to be widespread. Since no guidelines yet exist, it is not possible to evaluate these levels in terms of effects on benthic organisms. Chlorophenols have been identified as a concern, since in addition to being toxic compounds, they are also a potential source of dioxins (Health and Welfare Canada/Environment Canada 1983).

Concentrations of other chloroaromatics were consistently below detection limits and this data has not been presented. There appears to be little cause for concern over sediment accumulation of these compounds, at least on a province-wide basis, though site-specific conditions may dictate the need for consideration.

2. Sediment Influence on Bottom Water

2.1 Theoretical Considerations

The bottom water that is in contact with the sediment surface is a transition zone influenced by both the water column and the sediments. While movement of particles and contaminants commonly occurs from the water column to the sediments, through physical and chemical changes in the sediments this movement can be reversed. Under certain conditions, the sediments can act as a source to the water. If sediments are a significant source of contaminants to the water column, effects should be evident in the bottom water. The movement of contaminants from sediments to the bottom water through sediment desorption depends on the characteristics of the sediments and the chemical, as well as the physical characteristics of the overlying water (i.e., current velocity, and other factors affecting the resuspension of particulate matter).

One means of measuring the availability or reflux of chemicals from sediment to the water column is to determine the relative concentrations in each and assess whether the concentrations in the bottom water are more similar to the sediment concentrations (specifically, the porewater) or to the water column concentrations.

Perhaps the single most important factor affecting desorption of contaminants from sediment is the characteristics of the chemical itself. The solubility of a compound in water, and the affinity of a compound for the solid sediment fractions, as opposed to the aquatic phase, determine the strength of binding of the compound to the sediment. For many of the organic compounds, this can be measured by the partitioning behaviour and the result can be expressed as a coefficient such as K_{ow} or K_{oc} .

While the solubility or hydrophobicity of a compound determines the strength of binding to the various sediment fractions, the characteristics of the sediment itself can significantly affect desorption.

Larsson *et al.* (1990), for example, found that contaminated sediment in a Swedish river was a significant source of PCBs to the water column and noted that the desorption rate of the various PCB congeners was inversely related to the octanol-water coefficient such that those compounds with high K_{ow} had correspondingly low desorption rates. Desorption was also affected by temperature, though the most significant factor appeared to be the organic content of the sediments.

However, Larsson *et al.* (1990) also noted that in the Shiawassee River, concentrations in the water changed little before and after sediments contaminated with PCBs were removed, and the only significant increase was during the removal process, presumably as a result of the high level of sediment disturbance.

Wong *et al.* (1989) found that sediments can be an important source of aluminum to the overlying water under certain pH conditions, especially the monomeric species which are believed to be the more toxic species. Generally they found that in organic rich waters the species of aluminum are reactive and that the concentration and characteristics of the organic ligands determine the fate of the aluminum.

Once desorbed from the sediments, the form or phase in which contaminants persist in the water column can also vary and seems to depend on a number of factors.

Eadie *et al.* (1990), using radiolabelled hydrophobic organic compounds, found that in the water column the freely dissolved phase was usually dominant, while less than 5% of the compound was

associated with the dissolved organic matter phase. The amount in suspended matter was found to be variable and depended on the solubility of the compound. For the least soluble compounds tested, benzo[a]pyrene ($\log K_{oc} = 6.66$) and HCB ($\log K_{oc} = 6.76$) approximately 40% of the water column concentration was associated with suspended matter, while approximately 50% was in the freely dissolved phase. As solubility of the compound increased the concentration in the freely dissolved phase also increased while the concentration in the particle bound phase decreased.

Similarly, McCarthy and Black (1988) found that the partitioning of persistent organic compounds to dissolved organic matter (DOM) in systems where suspended particulate levels were high, accounted for only a very small amount of the contaminants. They concluded that failure to take into account partitioning to the DOM would result in only a small error.

Most discussions of desorption are theoretically based. Actual rates of desorption from sediments have rarely been calculated since these are highly variable and depend on a host of factors, such as sediment disturbance, binding intensity of the compound, the sediment type, pH and redox. For example, Karickhoff and Morris (1985) found a 4 to 6 fold increase in the water concentration of HCB when worms were present in the sediments. They attributed this increase to "irrigation" of the sediment by the worms, which enhanced the desorption of HCB from the sediment. Fry and Fisher (1990) found an increase in water concentration of PCB for similar reasons when midges (*Chironomus*) were present in the sediment.

The weight of evidence seems to point to sediments as a source of contaminants to the water, though the rate or amount released varies according to the nature of the sediment, the physical nature of the waterbody (re: physical disturbance of the sediment) and the characteristics of the compound. Due to the complexity of sediment-contaminant interactions, the effects of sediment bound contaminants are still largely not quantified.

2.2 Program Synthesis

A major concern that the In-Place Pollutants program sought to address was whether contaminant concentrations in the bottom water can be related to contaminant concentrations in the sedi-

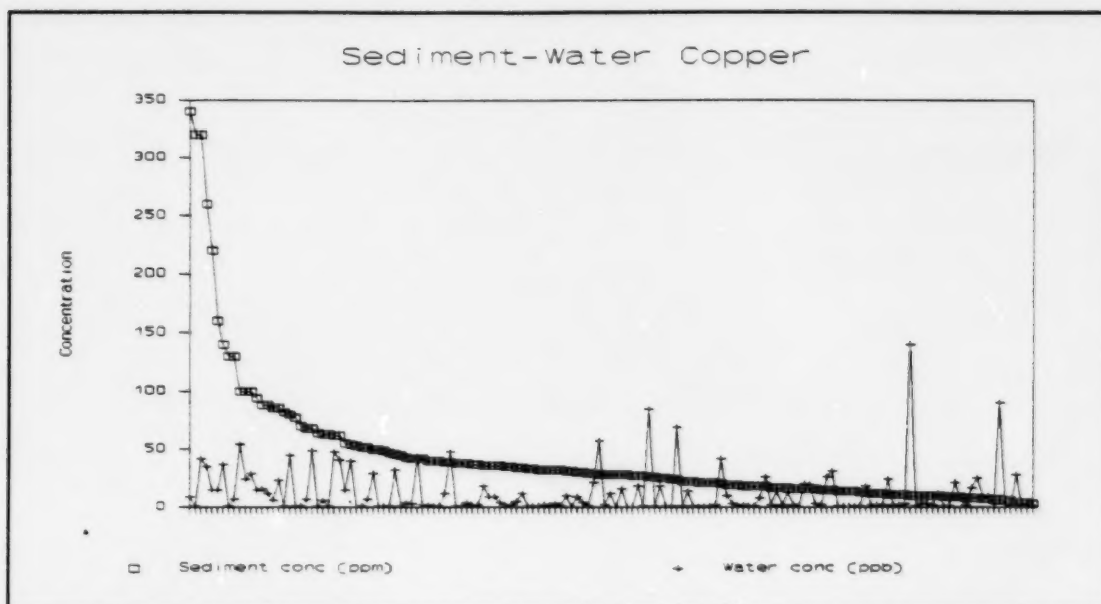


Figure 7: Copper in sediments and bottom water (plotted in order of decreasing sediment concentrations). Sediment concentrations in ug/g dry weight, bottom water concentrations in ug/L.

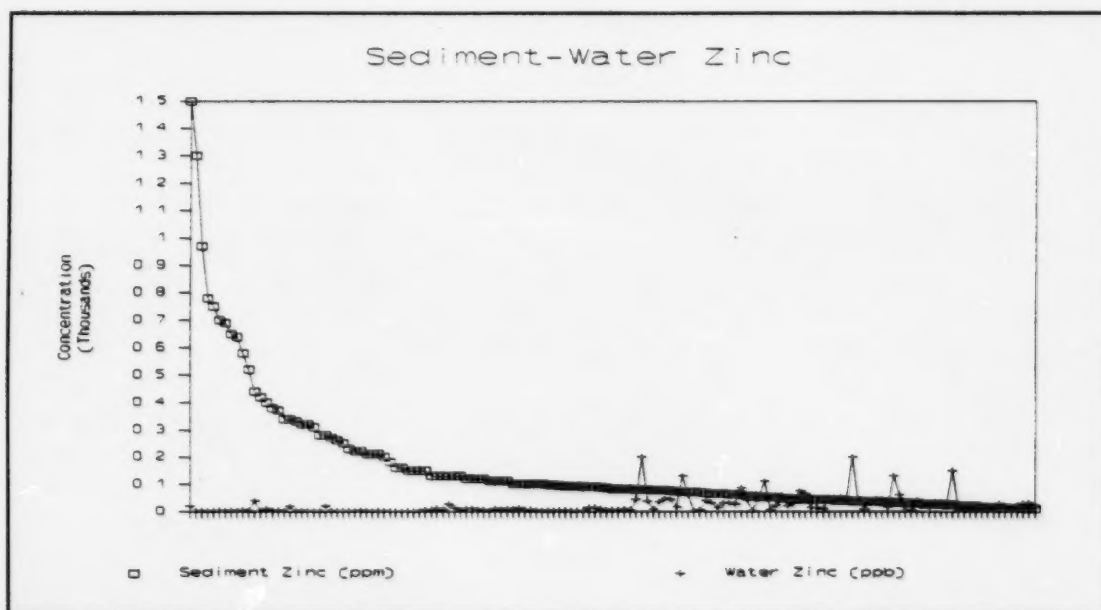


Figure 8: Zinc in sediments and bottom water (plotted in order of decreasing sediment concentrations). Sediment concentrations in ug/g dry weight, bottom water concentrations in ug/L.

ments. In order to answer this question, a correlation matrix of sediment and bottom water concentrations was constructed for all of the metals. From this matrix, the only correlations significant at the 95% level ($P < 0.05$) were for Iron ($r = .2261$), Pb ($r = .2193$) and Mn ($r = 0.2797$) (Spearman Rank Correlation). These results show no strong relationships between sediment metals and concentrations in the bottom water existed. Correlations were not attempted with organic compounds since concentrations in bottom water were generally below detection limits. Only in a few instances were there detectable levels in the water (Appendix, Tables 5 and 6).

A simple plot of bottom water metal concentrations with sediment metal concentrations did not yield any predictable relationship. In general, water concentrations were usually higher in those locations where sediment concentrations were high (see for example, Figures 7 and 8), though in some instances bottom water concentrations were below detection limits in areas of high sediment concentrations. As with uptake by biota, which is discussed in Section 4, the primary factor appears to be the potential for desorption of the compound from the sediment, as influenced by the sediment constituents and the nature of the chemical itself.

The lack of a relationship between sediment and water cannot be used to suggest that sediment concentrations are not related to water concentrations. This is true for two major reasons. First, the contribution of sediments to water column concentrations is likely to be minor in relation to other sources of input. In many of the locations, the sources responsible for the sediment concentrations have not been controlled, with the result that they are still contributing to the water column. It has not been possible in this study to separate or isolate the relative contributions from each source. Secondly, water concentrations are measured at one point in time while the sediment concentrations represent the cumulative concentration over an extended period of time.

The lack of a relationship does suggest that the sediments are not obvious major contributors to the water column. The indications are that if sediments are undisturbed, they are likely to be contributing contaminants to the water at a relatively slow rate, and, with the dilution provided by the overlying water, may not reach levels of concern until external sources are curtailed. Laboratory studies (Section 5.1) however, have shown that desorption can be significant when sediments are disturbed. The rate of release

depends on a number of factors such as the sediment organic content (TOC) and other physical characteristics such as resuspension rate, bioturbation or any physical process that could disturb the sediments and resuspend them into the water column.

One of the main concerns with sediment release of contaminants has been the effects on the water column organisms. However, as noted earlier, in many cases the sources that originally contributed to the problem have not been controlled, with the result that accumulation by biota, for instance, can not be attributed to just one route. These conclusions strongly favour source control as the major means of protecting sediment quality.

Since bottom water samples were usually taken 1 meter above the sediment surface, the analysis of the In-Place Pollutants Program data was problematic in relation to sediment uptake. Water samples may have been taken too high off the bottom in some cases, particularly in flowing water situations and thus may not have been truly indicative of actual conditions near the sediment surface.

Results of the IPP program do not provide any strong evidence as to whether sediments do act as a source of contaminants to the water. Areas of high sediment concentration did not always correspond to areas of high water concentration. However, sediments are likely to be sources under certain conditions, primarily when sediments have been disturbed.

Primary reliance must be placed on information from the literature, which is equivocal at best. The conclusion must therefore be that sediment can be a source to the water column under some circumstances. As discussed in the following sections, contaminant effects are often readily apparent on the sediment-dwelling organisms themselves.

3. Benthic Communities

3.1 Theoretical Considerations

Benthic community analysis (generally based on the presence/absence of benthic species, measures of community response such as diversity and species richness, and analysis of trophic or feeding group assemblages) is based on the concept that bottom-dwelling organisms respond to the factors, both physical and chemical, that affect their environment. The concept itself is not new. Richardson (1921)

based his detailed study of the condition of the Illinois River on the analysis of benthic communities. Since then, additional measures, such as various indices, have been developed to summarize the often complex information that has emerged from such studies.

Analysis of the species composition (in broad terms, the presence of certain species and often, the characteristic absence of others) and the relative densities of those present, form the basis of community structure analysis. This method of data interpretation takes as its foundation the classical ecological definition of a community as one that consists of a few species which are commonly distributed and present in greater densities, and a larger number of species that are sparsely distributed and relatively rare (Odum 1966). In a natural state such a community exists as a balance between these two groups. Under environmental stresses the natural balancing mechanisms are disrupted and an unnatural, stress-defined community or assemblage of species is favoured (Hynes 1960, 1970).

The analysis of functional feeding groups is similar to the above but considers the ecological role that each species plays in the habitat. These roles are defined on the basis of the trophic levels, and hence the energy sources the various members of the aquatic community utilize.

While the application of benthic community assessment to ecosystem characterization as originally used by Richardson considered only the effects of organic matter and the attendant physical effects such as de-oxygenation of the bottom water, it has been shown over the last 15-20 years that chemical contaminants in the sediment and water column can have effects on benthic communities that are similar to those of organic matter. Studies, such as those by Beckett and Keyes (1983), have shown that the effects of contaminants in sediment can be similar to the effects of organic matter: the elimination of sensitive species. However, they go on to observe that the opportunistic expansion of resistant organism populations that is characteristic of organic enrichment is generally lacking, suggesting that some toxic effects may be felt throughout the benthic community. Wiederholm *et al.* (1987) found that oligochaetes, usually the organisms most tolerant to organic enrichment, were susceptible to toxic contaminants. Chapman *et al.* (1982) also found that a number of oligochaete species commonly considered tolerant of organic enrichment were relatively more sensitive to chemical contaminants. Winner *et al.* (1980) found that the

community level response of a stream benthic community to metal contamination was different from the commonly observed response to organic enrichment. The impact of metal contamination differed in that all groups of organisms were affected, with no clear rise to dominance of any one group.

Despite the use of benthic studies as monitoring tools, one weakness has always remained. While benthic communities are now recognized as good indicators of community stress, they cannot be used to identify the specific agents responsible for the stress.

In order to pursue this point, many of the benthic studies of the last 10 years have also collected chemical data on the sediments and water column, and through multivariate statistical techniques have attempted to link changes in community structure with physical/chemical changes in the sediments. Most have met with only limited success. The reason generally lies in the close interconnection between sediment organic matter, the distribution of benthic species, and the distribution of contaminants. The presence of organic matter in sediments is a major factor affecting the suitability of a substrate for benthic organisms which in turn is often the principal factor governing the distribution of benthic organisms. In the absence of chemical contaminants, organic matter can result in the elimination of some organisms, usually those sensitive to the additional oxygen stress that organic matter imposes. Feeding mechanisms may also be a factor, resulting in the burial of food, or of the organism itself, the end result of which is suffocation. However, as shown in section 1.4, contaminants introduced to aquatic systems also have a high affinity for organic matter. The problems of this type of statistical analysis have typically been to separate the effects of the contaminants from those of the organic matter.

The finding that organic matter can effectively control the availability of some contaminants, suggests that toxicity of chemical contaminants, particularly organic compounds, in organic rich sediments should be lower than in organic poor sediments. The work by Di Toro *et al.* (1990) suggests that the sulphide concentration of sediments is mainly responsible for controlling metal toxicity in some sediments, while the organic content and the Fe/Mn hydroxides can be significant factors in sediments poor in sulphide. Sediment organic matter appears to assume much greater significance in the case of the nonpolar organics,

where organic carbon appears to be the principal controlling factor.

One of the difficulties with using animal populations is that under conditions of chronic contamination, some populations of organisms may be able to adapt, through evolutionary mechanisms, to the elevated concentrations. Klerks and Levinton (1989) suggest that differences in resistance of two populations of *Limnodrilus hoffmeisteri* from differently contaminated areas are due to the evolution of resistance in the population exposed to the higher metal levels in sediment.

Organisms vary in their sensitivity to chemical contaminants. Clements *et al.* (1988) found that in stream mesocosms and natural field conditions, mayflies (Ephemeroptera) were among the most sensitive to heavy metals (Cu and Zn), while some species of filter-feeding caddisflies (Hydropsychidae) were considerably more resistant. The elimination of the mayflies in both systems resulted in the proliferation and dominance of the Hydropsychidae. The feeding mechanisms of the hydropsychid caddisflies may play a part in this since these organisms live by filtering particles from the water and are not directly in contact with the sediments. Generally, they do not inhabit those areas favourable to the accumulation of fine sediment particles.

Leland *et al.* (1989), in an experimental dosing of a stream with copper, found that differences in sensitivity occurred among families in some orders of insects and that generally the herbivores and detritivores were more sensitive than the predators. However, this may also be linked to the behavioural and feeding habits of the different organisms. Both detritivores and herbivores are more likely to come into direct contact with higher concentrations of contaminants than predators, either as a result of physical contact with the sediment and porewater (many burrow in the sediments) or through ingestion of organic matter from the sediments. Predators are more likely to be exposed mainly through exposure to water at the sediment surface and through ingestion of contaminated prey.

Wiederholm *et al.* (1987), using sediment contaminated with heavy metals, found that both reproduction, and to a lesser extent, survivorship, in oligochaetes were negatively affected by sediment bound metals.

Some life stages of organisms have also been found to be more sensitive than others. McCahon *et al.* (1989) found that larvae of the caddisfly *Agapetus*

fuscipes were more sensitive to cadmium in the early instars than in the later instars. Gauss *et al.* (1985) found a similar response in chironomids (*Chironomus plumosus*) to copper stress. Fourth instar larvae were found to be 12 to 27 times more resistant than first instars.

There is also evidence that some organisms will actively avoid and escape contaminated areas. The presence of contaminants can also result in sublethal effects that may prevent the recolonization of such areas by organisms through either physiological or behavioural responses. McMurtry (1984) found that some species of oligochaetes (*Tubifex tubifex* and *Limnodrilus hoffmeisteri*) actively avoided sediments treated with CuSO_4 and ZnSO_4 . Others have found that the presence of contaminants can result in behavioural changes. Keilty *et al.* (1988) found that elevated levels of endrin in sediment resulted in attenuation of burrowing activity in *Stylogdrilus heringianus* and *Limnodrilus hoffmeisteri*.

3.2 Program Synthesis

Analyses of the IPP benthic results for each area studied (Jaagumagi 1988) found that there were differences in community composition based both on species assemblages and feeding groups and that these generally coincided with known sources of pollution. When the zones of effect, as measured by species composition or community responses, were compared with the sediment zones, the most obvious result was the close correspondence between the distribution of benthic communities and the distribution of sediment type. The distribution of fine sediments and organic matter appears to be the single most significant factor affecting benthic organism distributions. This is not surprising given the great amount of work that has demonstrated the strong benthic organism - substrate relationships that exist (Minshall 1984 provides a good review). Johnson *et al.* (1987) showed that substrate type was also a major determinant of the faunal composition within an area.

In those areas where impacts on benthic communities were apparent, there were identifiable zones of sediment contamination. However, in many cases the observed biological impacts could not be unequivocally attributed to contaminants in sediments, since there were still active sources to the water column. In most of the highly impacted areas for metals, such as Humber Bay and the St Mary's River, there are still active sources and the benthic community response is likely a combined response

to contaminants in both the sediment and the water column. In the St Mary's River, the benthic community below the Algoma Steel mill outfall was severely reduced, but sediment contaminant concentrations were not substantially different from areas further downstream. The benthic response in this case appears to be related to the water column, more than to the sediments. In the Otonabee River/Rice Lake system, however, there was no apparent effect on the benthic community from high sediment concentrations of both PCBs and PAHs. This is not unexpected, however, since the affinity of organic compounds for organic matter in sediments can render them unavailable, and thus reduce their potential toxicity.

Overall, the most clearly defined effects of sediment on benthic communities, both in terms of effects on species composition and feeding group composition appeared to be the effects of sediment contamination by organic matter. In virtually all areas studied, an increase in sediment organic matter was accompanied by a shift in benthic communities to a fauna reduced in diversity and taxonomically dominated by the oligochaetes and chironomids.

The reduction of the benthic data to numerical indices did not provide any correlation with contaminant concentrations in the sediments. Presumably this is due to the strong effects that sediment composition has on the benthic organism distributions. The use of indices however, ignores some of the subtleties in the benthic data, resulting in a reduction in overall resolving power of this approach. Differences in density and diversity of specific groups of organisms, that may be significant, are ignored when data are reduced to indices. Multivariate analysis, which would be more useful for this type of data, suffers from the presence of other, so-called "nuisance variables", such as sediment type and organic matter content, that can have a pronounced effect on benthic organism distributions. These factors can obscure relationships, or provide false evidence of relationships, simply by the connection of two variables such as benthic community composition and sediment contaminant concentrations through a third such as sediment type or organic content.

Benthic community analysis, because of the type of data involved, inherently lends itself primarily to site-specific analysis. While the presence of organic matter was the single, largest factor affecting benthic communities, contaminant effects could be inferred from this data in areas of severe sedi-

ment contamination, though the picture was often confounded by the presence of water column effects. The benthic data serve mainly to determine the specific effects of contaminants on benthic community patterns under the conditions prevailing at each site. Site specific evaluation of benthic communities are included in Volume V of the In-Place Pollutants Program (Jaagumagi 1989) and the reports on the individual MISA Pilot Site studies (Jaagumagi *et al.* 1990, 1991).

The pattern of community response was similar in most of the areas studied. The principal response was a reduction in diversity as organic matter content increased. The benthic community was generally reduced to a few species of oligochaetes and chironomids, some clam species and some crustaceans. Additional stressors further reduced the communities in some areas to one or two species of oligochaetes and a similar number of chironomids. The stressors were generally organic matter inducing low oxygen content in the sediments and bottom water, and chemical contaminants. Where the effects were due primarily to reduced oxygen content, as a result of the decomposition of organic matter, the surviving populations often expanded to extremely high densities. For example, the density of oligochaetes in the Kam River below the turning basin was 400,000 to 500,000 individuals per square meter. Upstream densities in this same river were approximately 3,000 per square meter.

When contaminant effects are superimposed on a high organic matter content, as is often the case with contaminated sediments, the principal effect is a reduction in the density of organisms which is not accompanied by any increase in diversity. Often the diversity is also reduced further, due to toxic effects of the contaminants. A major difficulty encountered in these studies was the effect that organic enrichment, through oxygen depletion, had on the benthic fauna. In many of the study locations the benthic fauna was already reduced to a few species that were particularly tolerant of these conditions. The co-occurrence of chemical contaminants and organic matter tended to obscure the effects of the contaminant except in cases of severe contamination, since the more sensitive indicators of contaminant stress had already been eliminated. At high sediment contaminant concentrations, the tolerant fauna was noticeably affected, while at moderate levels of contamination, the effects would be more subtle and not readily distinguishable from substrate effects.

4. Contaminant Uptake by Biota

4.1 Theoretical Considerations METALS

Metal behaviour in natural environmental systems is governed by a number of factors such as acidity, the presence of various complexing ligands, the form of the metal, the nature of the sediment, and amount of dissolved oxygen (Forstner and Wittman 1983). All of these factors play important roles in the distribution of metals in sediments and their availability to organisms.

Accumulation of metals from sediments by aquatic organisms has been postulated to occur through a number of environmental pathways. The most significant of these appear to be ingestion of sediment-bound metals and adsorption of free metal ions from interstitial water (Luoma 1989). While the latter appears to be the most significant, both these routes can contribute to significant metal residues in organisms, depending on the species of organism and the metal involved (Luoma 1989).

Clearly, when organisms come into contact with sediment-bound metals they are not exposed to these as a single entity but, rather, are exposed to a variety of metal-ligand associations that may change over time, or from place to place. Organisms are exposed to sediment-bound contaminants not only through surface exposure, but also through ingestion, either accidental or intentional (Luoma 1985; Hare *et al.* 1991).

Differences in organism exposure are possible depending on the life history and feeding habits of the organism. Those species that are primarily epibenthic are generally only in contact with the surface of the sediments, which are often well oxygenated and hence most contaminant release from the sediments and subsequent uptake by organisms occurs under oxidizing conditions. Other species, such as those that burrow in the sediments, can come into contact with the reducing conditions that usually exist below the thin oxidized layer (Luoma 1985). Since the concentrations in the more available fractions can also change under anoxic conditions, this may result in those organisms that feed at depth in the sediment being exposed to less available contaminant than sediment surface feeders (Hart and Andrews 1991).

As shown in the previous section, the binding of contaminants to certain sediment fractions or components can potentially affect their availability

to bottom-dwelling organisms. For example, Luoma and Bryan (1978) suggested that the availability of some metals can be enhanced at low concentrations of Fe, since less of the metal would be bound to the Fe/Mn oxides/hydroxides. Availability of others, for example mercury, which has a high affinity for organic matter, could be controlled by sediment organic matter content.

Despite these factors, the water column continues to be a very important source of contaminants to organisms. The mechanisms of uptake elucidated so far strongly suggest that the free metal ion can be most efficiently transported across cell membranes. The evidence to date suggests that uptake from ingested material via the gut requires dissociation of the compound to free ions and ligands before the metal can be incorporated from the gut. Luoma (1983) noted that the gut pH of most invertebrate was around pH 6, and would not be very efficient at removing metal ions from the associated sediment particles.

Since metals also occur naturally in sediments they present a special problem in determining modes of uptake. Luoma (1989) notes that for each metal there exist sediment bound forms that can be accumulated through ingestion of sediment, but that forms also exist that show little availability when ingested. In general, a number of studies have suggested that the free metal ion in the water, rather than the sediment bound species, is the most available form, and that uptake is most likely through adsorption from external body surfaces (gills, skin/integument)(e.g., Luoma 1983). Nalepa and Landrum (1988) have noted that while free metals are readily available for uptake, they tend to complex very strongly with the organic fraction in sediments and water, which limits their availability, at least in those cases where organic content of the water or sediments is high. Luoma (1989) notes however, that while metal assimilation from ingested sediment particles is much less efficient than from free ions in solution, the sediment source is much more concentrated and thus may contribute greater amounts to an organism's body burden than adsorption from solution. Nalepa and Landrum (1988) have observed that most metals require an active or facilitated process for assimilation and that accumulation from sediments is therefore most likely to be via ingestion.

Luoma (1983) noted that only for those metals considered essential micronutrients (zinc and to some extent, copper) did tissue residues appear to behave independently of environmental concentra-

tions. Clearly, no consensus yet exists on which pathways are the most significant in the accumulation of metals by aquatic organisms. Perhaps the best summary is that made by Luoma (1989) who states that "bioaccumulation from food can be significant for some elements and some species". The most important factors seem to be those governed by local conditions - i.e. organic matter content of the sediment and the presence of scavenger compounds such as the iron and manganese oxides and hydroxides. Which of these sediment components a metal partitions to in great measure seems to be dictated by the relative abundances of each in a particular sediment.

What does emerge from the great amount of work done on the uptake of metals by biota is that no one sediment component controls the availability of a metal to aquatic organisms. Rather it appears that sediment components, such as organic matter, sulphides, and iron and manganese oxides and hydroxides all influence availability from sediments (Forstner and Wittman 1983). In large measure, the work outlined in this phase of the In-Place Pollutants program supports these observations.

Factors that influence the release of metals from the sediment are likely to have the greatest potential effect on uptake. As noted in earlier sections, both physical and chemical factors can influence the movement of metals out of the sediments. Riedel *et al.* (1989) found that there was a measurable release of contaminants (arsenic) from sediments when burrowing organisms were present, and that the life history of the organism and its feeding habits resulted in different rates of release for different organisms. Generally, they observed that smaller actively burrowing organisms were more efficient at causing direct release of substances from sediment than were larger more sedentary organisms.

Studies have also shown that differences exist in the ability of organisms to accumulate and depurate metals. Zinc and copper are essential micronutrients and mechanisms for their regulation apparently exist in a number of species. Regulation in most of these species appears to take the form of an increased rate of depuration in areas of high environmental concentrations to match the rate of uptake (Rainbow and White 1989; Luoma 1983). Most organisms do not appear to be able to regulate the uptake of nonessential metals, and uptake appears to be dependent primarily on environmental concentrations (Luoma 1983).

The formation of insoluble metal sulphides in sediments also appears to affect the toxicity of metals to benthic organisms. DiToro *et al.* (1990) found that a reactive pool of solid phase sulphide (AVS) that exists in most anoxic sediments can reduce the apparent toxicity of metals through the formation of metal sulphides. The amount of sediment sulphide appeared to be directly, and inversely, related to the toxicity of the metal. They found that test organisms were able to tolerate a much higher sediment cadmium concentration when sulphide was present. In fully oxidized sediments, and even in partially oxidized sediments, the sulphide concentrations would be very low and the sediment sulphide would have no effect on binding of metals. Under these conditions, binding and effective removal of a metal would depend on other sediment constituents such as organic matter and Fe/Mn hydroxides.

In summary, the factors that can most enhance the release of metals from sediment are changes in redox, changes in pH, and physical disturbance of the sediment.

ORGANIC COMPOUNDS

The behaviour of organic compounds in sediment is intimately dependent on the nature, primarily the chemical stability, of the compound. Ionizing compounds in general behave similarly to the metals, and can partition to a number of sediment components (Smith *et al.* 1988). The nonpolar compounds (basically those that do not dissociate in solution) appear to behave in a much simpler fashion. These compounds partition primarily to the organic components of the sediment and water, with only minor amounts entering into solution. The behaviour of these compounds can be defined by the partition coefficient of the compound, which is the ratio of the amount of a compound that partitions to the water over the amount that partitions to an organic solvent (Smith *et al.* 1988). The solvent generally used is n-octanol. Compounds with high partition coefficients (generally expressed as the log of the ratio) are considered hydrophobic, with a high affinity for organic matter (among which is included animal lipids) (Witkowski *et al.* 1987). These compounds partition very strongly to organic matter and are also closely dependent on the size of the particles. Generally, sediment organic-matter content increases with decreasing particle size, with the highest concentrations of sorbed contaminants commonly found in the silt and clay fractions (Witkowski *et al.* 1987). There is some evidence that the nonpolar organics can also sorb, to a small

degree, to some of the mineral components of sediment, though sorption may actually be due to the organic coatings on some of these particles (Witkowski *et al.* 1987).

Uptake of these compounds by organisms appears to be relatively complex, despite the near singular attraction of these compounds to sediment organic matter. Availability of the less hydrophobic compounds would appear to be highest, since the relatively greater amounts available in the water (and this includes the sediment interstitial water) would suggest that these compounds could be accumulated to relatively high levels in tissues, though this is counteracted by the reduced lipophilicity of these compounds. Nalepa and Landrum (1988) have suggested that the predominant route of uptake of organic compounds appears to be through passive diffusion from the aqueous phase, generally across the integument or respiratory surface.

In contrast, Fry and Fisher (1990) have suggested that uptake of hydrophobic organic compounds is through both adsorption and ingestion. They also found that passive uptake contributed to tissue residues, but this did not appear to be a particularly significant route.

While compounds with low partition coefficients ($\log K_{ow}$ generally below 4) tend to be accumulated more readily, they also appear to be eliminated more rapidly as well. Those compounds that bind very strongly to sediment organic matter (characterized by $\log K_{ow}$ greater than 7) also do not appear to be accumulated to high levels. Due to the extreme hydrophobic nature of these compounds, binding to the sediments is very strong, thus decreasing the potential availability of these compounds to aquatic organisms. Additionally, the large molecular size of these compounds makes it difficult to transport them across membranes (Smith *et al.* 1988).

Those compounds with partition coefficients in the range of $\log K_{ow}$ 4 to 7 are generally the most likely to be accumulated to significant levels in organisms. These contaminants are eliminated relatively slowly in relation to their rate of uptake and thus are accumulated, to varying degrees (Smith *et al.* 1988).

Despite the simpler chemistry of these compounds in sediment, the routes of uptake still cannot be clearly delineated. Availability and, hence, uptake of these compounds can be from both the water (adsorption of the solubilized fraction directly from

the water (water column or sediment interstitial water)) or through ingestion of sediment contaminated with the compound (absorption through the gut) (Adams 1987). Both routes of uptake are dependent on a number of physical and chemical factors, both in the sediments and in the organisms, as well as the attributes of the chemical itself. For a number of compounds, including the polycyclic aromatic hydrocarbons (PAHs), the data suggest that the relative contribution from each depends on the relative concentration of the compound, its specific properties, and the life habits of the organism (Nalepa and Landrum 1988). In the case of PAH for example, when sediment concentrations are low, a substantial proportion of the organisms body burden seems to be acquired from the water, but when sediment concentrations are high, much of the PAH may come from the sediment.

Uptake of hydrophobic contaminants can be mediated by the presence of organic carbon, though the effect of this can also be variable. Nebeker *et al.* (1989) found that while the addition of organic carbon effectively reduced the toxicity of DDT in spiked-sediment, organic carbon had no effect on the toxicity of endrin.

McElroy and Means (1988) concluded, as a result of their experiments, that uptake is influenced not only by sediment organic matter (TOC) and organism lipid content, but also unmeasured intrinsic properties of the sediment and biological properties of the organism.

One of the biological properties influencing uptake of compounds from the various environmental compartments appears to be the organisms life history and feeding strategies. Muncaster *et al.* (1990) for example, found that the water phase appears to be the major route of uptake for clams. Elder and Matraw (1984) found no correlation between sediment concentrations of organic compounds and tissue residues in the clam *Corbicula manilensis*.

Essentially the uptake of organic compounds also depends on the efficiency of organism tissues as a sink for the specific compound as compared to sediments. Schuytema *et al.* (1990) for example, found that for hexachlorobenzene (HCB) sediments appeared to be a more efficient sink than organism tissues. This suggests that the water phase is the principal route of uptake, at least for this compound. Gabric *et al.* (1990) have suggested, through development of an uptake model, that accumulation is through consecutive partition equilibria between

sediment and interstitial water and then between interstitial water and organism tissue (lipids).

While the PAH compounds behave similarly to the organochlorines, there appears to be an essential difference between the two. Since PAH compounds can be metabolized by some benthic organisms, the tissue residues commonly measured may not be truly indicative of the availability of these compounds from their environment.

Varanasi *et al.* (1985) found distinct differences in the uptake of PAHs in various organisms and attributed differences in body burdens to differences in feeding strategies, depuration rate and biotransformation. As with other hydrophobic compounds, availability from the sediment appears to be governed by the characteristics of the specific compound as well as the characteristics of the sediment, primarily the organic carbon content.

McElroy *et al.* (1987) suggested that it was likely that deposit feeding organisms would accumulate both the PAH compound and the metabolic products from the sediments. McElroy *et al.* (1989) suggest that the principal route by which organisms accumulate PAHs is from the water and that desorption from sediments plays a significant role.

In summary, the release and subsequent uptake of organic compounds appears to be primarily a function of the strength of binding of the compound to sediment components. The nature of the compound itself is therefore the major factor and release of organic compounds depends much less on the physical alterations, such as changes in pH or redox, that so readily influence metal interactions.

4.2 Program Synthesis

METALS

The present study was undertaken to determine whether a predictable relationship exists between sediment contaminant concentrations and organism tissue residues at the study sites, and secondarily, what factors control the availability of these metals.

Studies on the numerous sites involved in the In-Place Pollutants program show that while sediment concentrations of metals were very high at some locations, these were generally not matched by tissue concentrations. While mechanisms for limiting uptake do appear to exist for some of the metals in a majority of the benthic organisms, as discussed

earlier the primary factor seems to be the availability of the compound from the sediments.

The results of the In-Place Pollutants Program are generally in accordance with observations from the literature (e.g., Luoma, 1989; Campbell *et al.* 1988) which have noted a distinct lack of a relationship between organism tissue residues and bulk sediment concentrations. Given the large number of factors that can affect availability from the sediments, this can be attributed to numerous factors.

Biota-sediment concentration ratios (BSCRs) are presented in Table 8 (Appendix). BSCRs were calculated on the basis of tissue residues calculated on a wet weight basis, converted to dry weight and corrected for gut contents using the formula in Persaud *et al.* (1987), and contaminant concentrations in sediment, expressed on a dry weight basis. Since the biota levels are a factor of uptake from both sediment and the water column (though the contribution from the latter is likely to be minor in the case of sediment in-fauna) the term bioconcentration has been avoided. For sediment in-fauna, this ratio can be used as an expression of the availability of contaminants from the sediments. A high ratio (>1) denotes that levels in organism tissue were higher than levels in the sediments and suggests that availability from these sediments is high (the use of a BSCR makes no assumptions regarding the actual route of uptake from the sediments). A high concentration ratio does not necessarily imply high tissue levels but merely measures tissue levels relative to sediment levels.

For most metals these ratios varied inversely with sediment organic matter, suggesting that sediment carbon effectively reduced the availability of the metals to benthic organisms. The BSCRs must be used with caution since despite the relatively low concentration ratios obtained for samples from the most contaminated sites, total invertebrate tissue residues of some metals (Cu, Cr, Fe and Pb) were actually highest in organisms from these locations.

Typically, the highest BSCRs were in sediments low in organic carbon (as TOC). From the data, certain generalizations can be made regarding uptake of metals and the presence of organic carbon. Where sediment concentrations of a contaminant were high, and TOC concentrations were

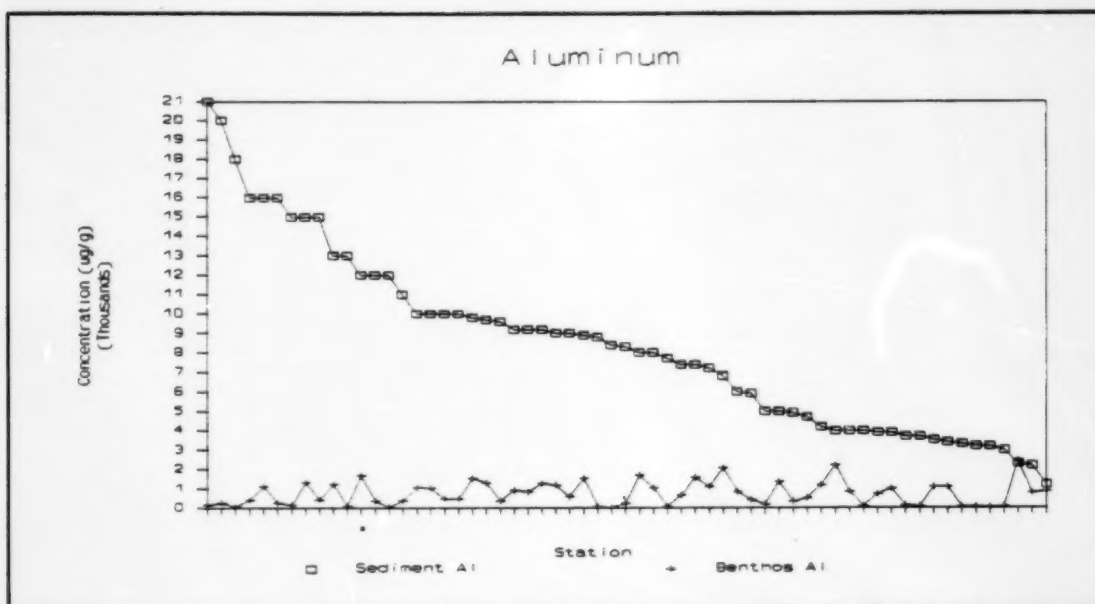


Figure 9: Aluminum concentrations in sediments and benthic invertebrates (plotted in order of decreasing sediment concentration). Sediment concentrations in ug/g dry weight of sediment, tissue concentrations in ug/g wet weight of organism.

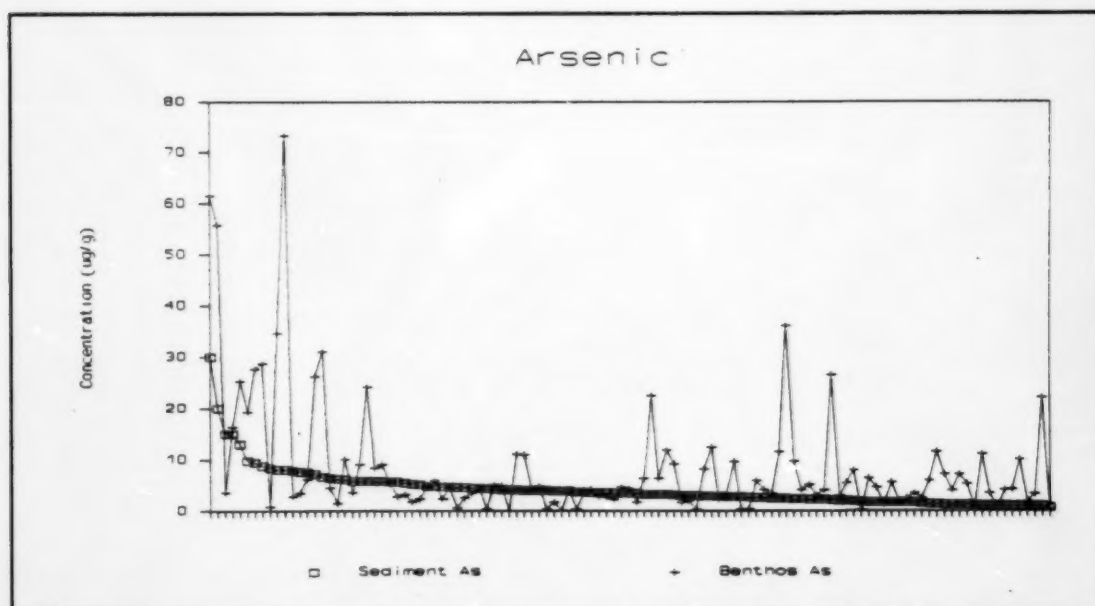


Figure 10: Arsenic concentrations in sediment and benthic invertebrates (plotted in order of decreasing sediment concentrations). Sediment concentrations in ug/g dry weight of sediment, tissue concentrations in ug/g wet weight of organisms.

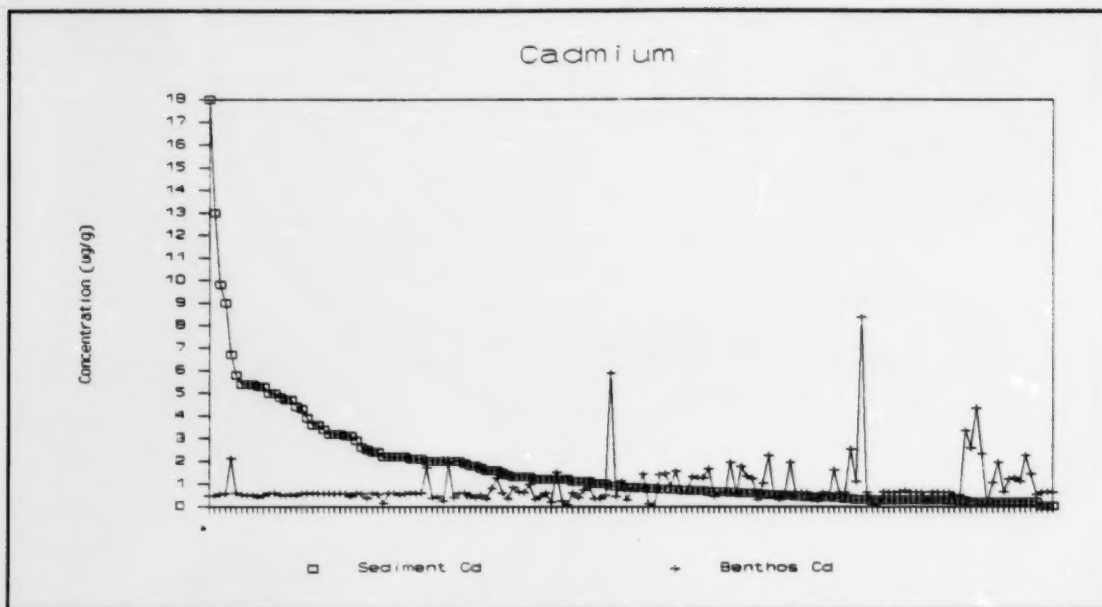


Figure 11: Cadmium concentrations in sediments and benthic invertebrates (plotted in order of decreasing sediment concentrations). Sediment concentrations in ug/g dry weight of sediment, tissue concentrations in ug/g wet weight of organisms.

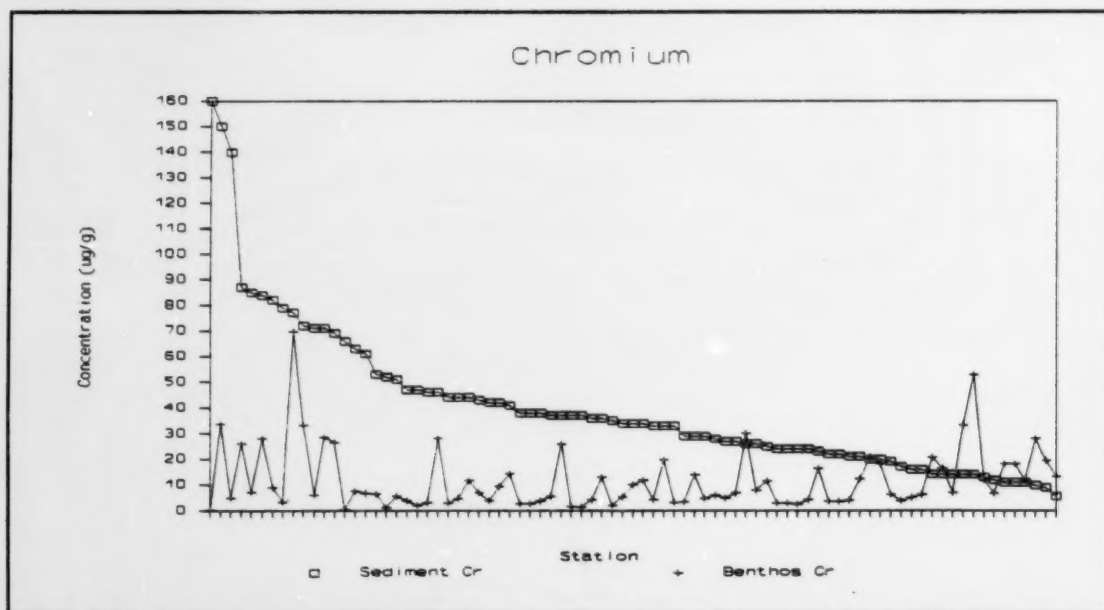


Figure 12: Chromium concentrations in sediments and benthic invertebrates (plotted in order of decreasing sediment concentrations). Sediment concentrations in ug/g dry weight of sediment, tissue concentrations in ug/g wet weight of organisms.

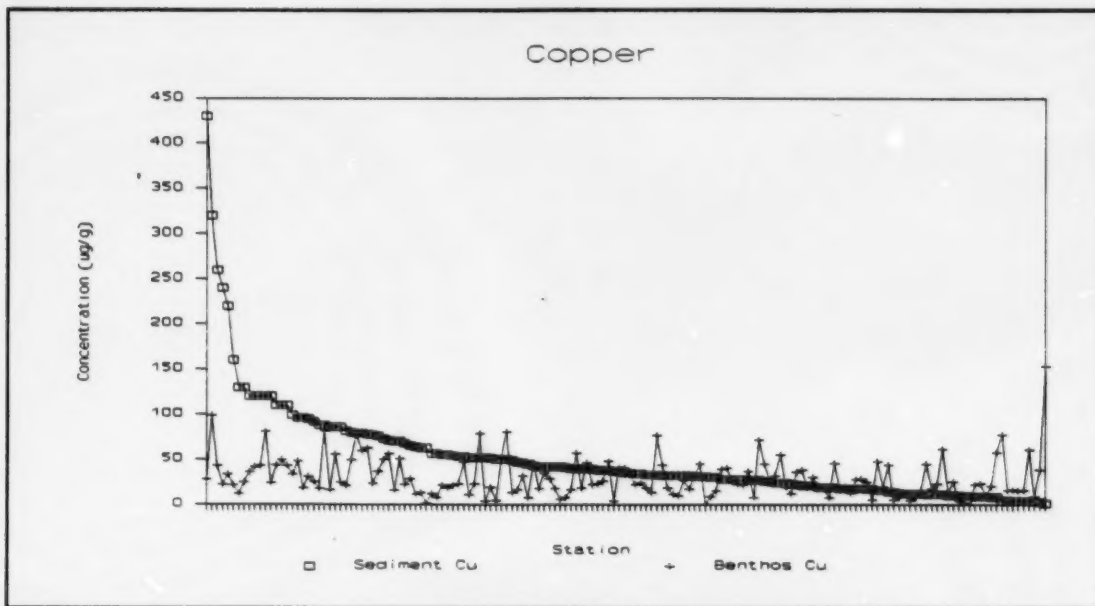


Figure 13: Copper concentrations in sediments and benthic invertebrates (plotted in order of decreasing sediment concentrations). Sediment concentrations in ug/g dry weight of sediment, tissue concentrations in ug/g wet weight of organisms.

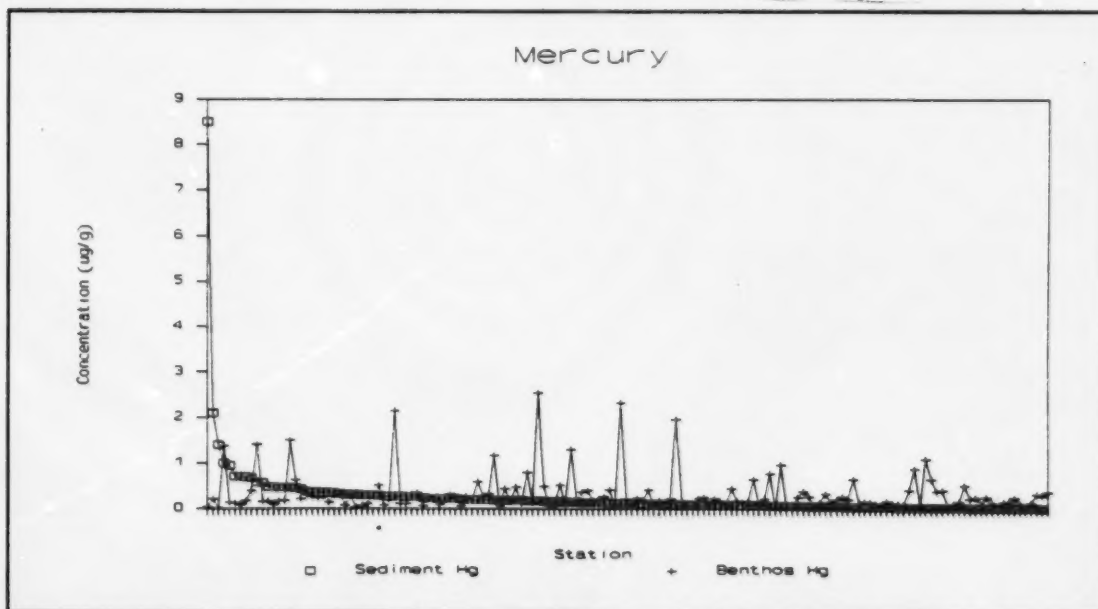


Figure 14: Mercury concentrations in sediments and benthic invertebrates (plotted in order of decreasing sediment concentrations). Sediment concentrations in ug/g dry weight of sediment, tissue concentrations in ug/g wet weight of organisms.

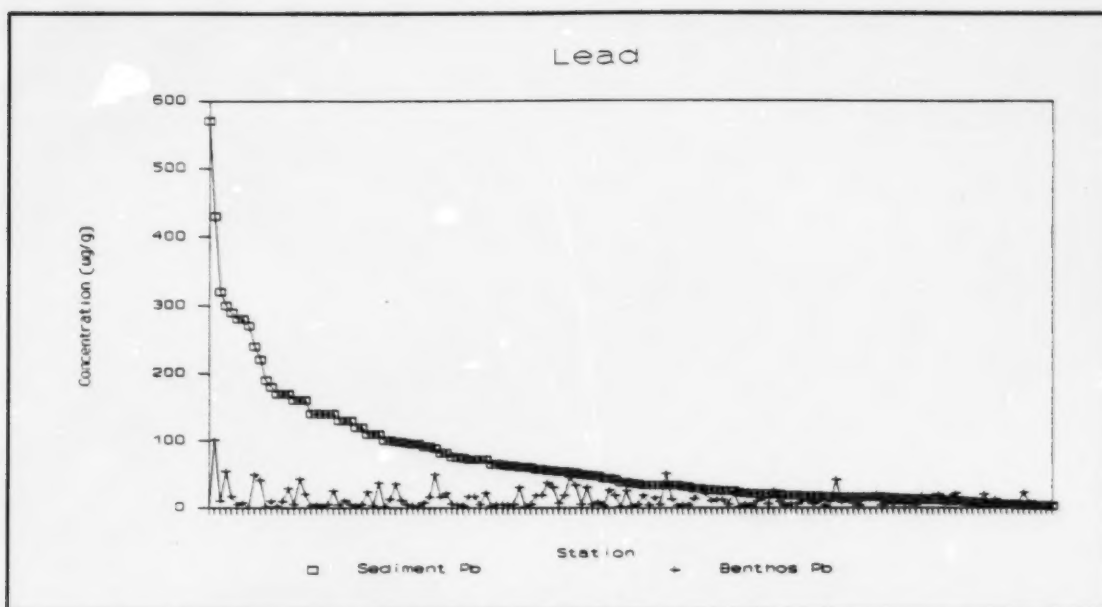


Figure 15: Lead concentrations in sediments and benthic invertebrates (plotted in order of decreasing sediment concentrations). Sediment concentrations in ug/g dry weight of sediment, tissue concentrations in ug/g wet weight of organisms.

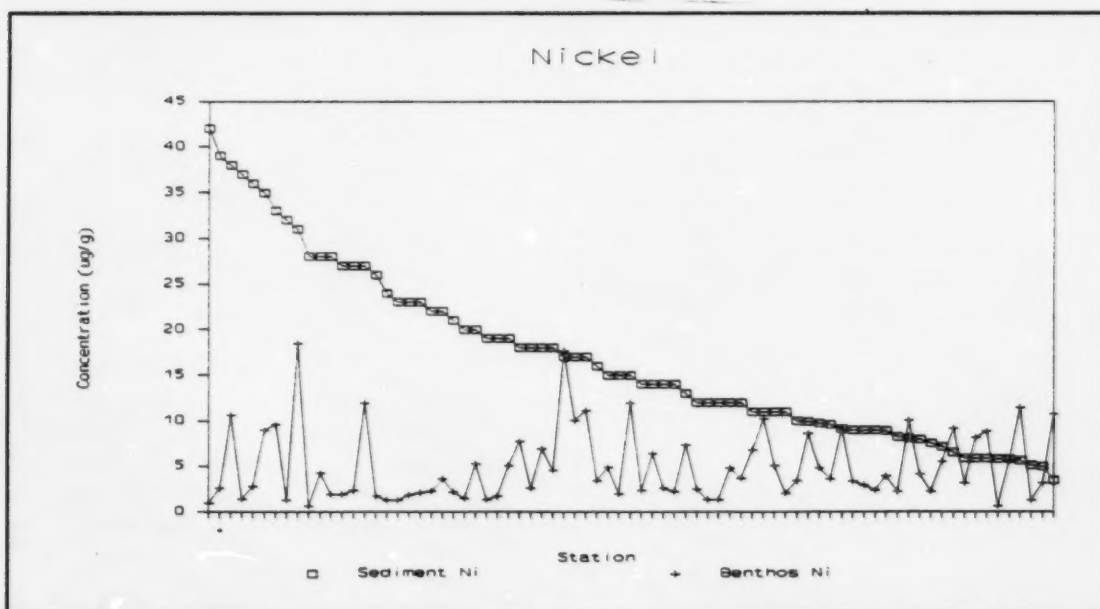


Figure 16: Nickel concentrations in sediments and benthic invertebrates (plotted in order of decreasing sediment concentrations). Sediment concentrations in ug/g dry weight of sediment, tissue concentrations in ug/g wet weight of organisms.

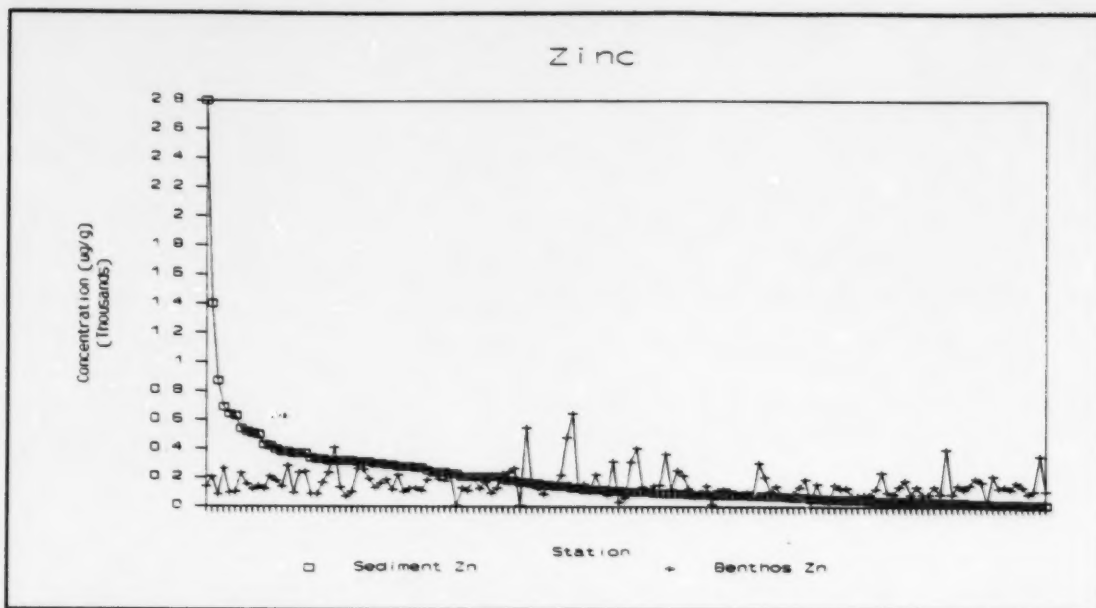


Figure 17: Zinc concentrations in sediments and benthic invertebrates (plotted in order of decreasing sediment concentration). Sediment concentrations in ug/g dry weight of sediment, tissue concentrations in ug/g wet weight of organisms.

also high, tissue residues and BSCRs were low, suggesting that uptake was low due to low availability from the sediments. Where sediment concentrations of a contaminant were low and TOC was also low (as in sandy sediment), tissue concentrations were generally also lower in relation to the more contaminated areas. However, tissue residues in relation to sediment concentration were high and BSCRs were typically above 1 and often much higher. While this may suggest increased availability from the sediment, it could also indicate that water concentrations contributed a relatively larger amount to organism tissue residues. Finally, in those areas where sediment concentrations were relatively high and sediment TOC was low (an uncommon occurrence, given the co-occurrence of contaminants and organic matter), tissue residues were also high, and this is perhaps the strongest evidence in the study that organic matter can exercise some control on availability from sediments.

In the course of the In-Place Pollutants data analysis it was found that tissue metal residues in benthic organisms did not vary in direct response to sediment concentrations. A plot of benthic organism tissue residues with corresponding sediment concentrations (the latter plotted in order of decreasing concentrations) showed that most of the tissue residues occurred within a certain concentration range, though considerable variability was evident within this range (see Figures 9 through 17). An estimation of a line through these points yields a

nearly horizontal line, suggesting there is no apparent relationship and further suggests that there may be some limit on uptake. In particular, there was no noticeable increase in tissue residues where sediment concentrations were high (Figures 9-17). The apparent rise in the BSCR therefore appears to be principally due to the decrease in the sediment concentration relative to tissue residues, and not to an increase in the tissue levels.

Table 7 (Appendix) lists tissue residues for metals in benthic organisms. While the highest residues were often in those organisms from the most contaminated study locations, the stations at which the highest tissue residues were measured were usually not the most contaminated.

Hart and Andrews (1991) found no strong statistical relationships between sediment concentrations and tissue residues, and even expressing sediment concentrations on a per gram carbon basis or a sediment iron/manganese hydroxide basis yielded only slight improvements in correlation. The uptake of metals by benthic biota appears to be influenced by other factors in addition to the bulk sediment concentration of a contaminant.

In the next step, Hart and Andrews (1991) correlated tissue residues with the concentrations in the various sediment fractions. Again, there was no apparent relationship between any of the sediment fractions and tissue residues. Thus, the potential

availability from the various sediment fractions does not appear to be a principal factor influencing the uptake of metals, at least in the In-Place Pollutants Program sites. As noted earlier in the theoretical discussion, it appears that tissue residues are influenced by a number of different factors and that no simple relationship exists between tissue residues and concentrations in a single environmental compartment.

Tissue residues were also correlated with sediment concentrations in both bulk sediments and the individual sediment fractions at individual sites, though no statistically significant relationships were observed on a site-specific basis either.

It is apparent from the In-Place Pollutants study that tissue residues of heavy metals are not predictable from bulk sediment concentrations and only marginally less so from sediment geochemical fractions (for metals). Normalization to TOC, Fe/Mn hydroxides, or both, did not increase the predictability of the relationships. Organic-bound metals thus appear to be only one part of the complex mechanism of metal uptake by biota that also includes the iron/manganese oxide bound fractions, possibly also the carbonate-bound fractions (though this is usually small), and, as recently suggested by DiToro *et al.* (1990), the sulphide-bound fraction. The latter two were not tested in this study. Evidently, no simple relationships exist between sediment concentrations of metals and tissue residues. As indicated by other studies, tissue residues will likely depend on the interaction between sediment concentrations and water concentrations, as mediated by such factors as sediment organic matter, redox potential, pH, and dissolved organic matter (DOM).

Tissue residues appeared to be most strongly influenced by environmental concentrations, since the greatest accumulation of contaminants in tissues occurred in areas of highest environmental accumulation.

Analysis of contaminants in sculpin tissue was seriously hampered by the lack of comparable data between stations. Sculpins were collected by hand by divers from suitable habitats though these did not always coincide with the sediment and benthic sampling locations, but were within the same general area. Therefore, the data available for many locations includes fish collected at sites close to, but not identical to those from which benthic organisms were collected. Since the principal differences between these sites would be the presence of

organic matter, it stands to reason that the sculpins, collected in areas of much lower TOC (generally rock or gravel substrates) would potentially be exposed to much lower sediment concentrations. Similarly, the ingestion of prey organisms from these sites would also potentially result in lower tissue residues. In addition a number of different age classes were collected, distributed over a number of different species, as well as a hybrid, in the study area. Interpretations made from this data are, therefore, incomplete and may even be misleading when applied to individual sites. Any conclusions based on sediment availability must be interpreted with the utmost caution since sediment concentrations at the sediment sampling locations are likely to be quite different from sediment concentrations at the sites at which the sculpins were collected.

In general, tissue levels of metals in sculpins could not be related to any specific source. Tissue levels varied only slightly between stations. In many cases, the tissue levels of metals in fish were lower than levels in benthic invertebrates. Because of the sample design it cannot be determined whether these differences are due to differences in rate or modes of uptake, or whether these are simply due to different potential exposures due to differences in sediment concentrations between the areas from which each were collected. Therefore it is not clear on the basis of a simple comparison whether sediments do play a role in increasing the availability of metals to benthic organisms, especially the sediment infauna. For benthic organisms, the most likely mechanism would be through desorption of the metal from the sediments to interstitial water, though ingestion appears to also be a significant route for at least some metals under certain conditions. Studies have shown that levels of contaminants in the interstitial water are usually more similar to sediment concentrations than to water column concentrations (McElroy *et al.* 1989). In addition, desorption from the solid sediment fractions to the interstitial water could provide a more constant supply of contaminants than the water column, which would depend primarily on autochthonous input. Such differences in exposure could readily account for differences in uptake patterns between these two groups of organisms.

Levels of some metals were similar in both sculpin and oligochaete tissues and may suggest that the water column rather than the sediment is the principal route of uptake.

The testing of individual sediment fractions yielded the best correlations between the F4 fraction

(Fe/Mn oxide/hydroxide bound) and tissue residues. Normalization by iron oxide provided the most significant improvements in relationships. Tissue residue-sediment relationships for the fish were stronger for some of the metals than for benthos, though it is questionable whether these relationships are meaningful, given the differences in sampling areas of both.

The correlation of tissue levels with levels in the F4 fraction may be partially explained by the fact that in the sediment, metals bound to the F4 fraction are usually only released under anoxic conditions. Further, the concentration of a metal in the F4 fraction is dependent on the concentration of the metal in the water column, since iron and manganese oxides and hydroxides in the water column act as scavengers of other metals (though this is also partially dependent on the iron concentration of the water). The suggestion that the free metal ion in water is the most readily assimilable source in the water may explain the higher correlation of organism tissue residues with levels in the F4 fraction, since free ions in the water would be a source of metals to both sediment and organisms. The lower correlation of concentrations in the F4 fraction with benthic tissue residues, suggests that sediment release of these metals, except under anoxic conditions, is not a major route of uptake for benthic organisms.

Hart and Andrews (1991) found that those models that attempt to include a number of sediment sources, such as those developed by Shea (1988) and Tessier *et al.* (1984) which have included factors for Fe and Mn oxides, resulted in no improvement in correlation in this study. In general, these models were inferior to the normalized F4 sediment fraction as trace metal predictors.

It is important to note that Fontaine (1988) observed that statistical models, while able to address questions about fate and effects of contaminants in aquatic systems are strictly empirical and they make no attempt to use biological, chemical or physical theory to define a functional relationship. Thus statistical relationships can only provide indications of where a biological relationship may exist.

ORGANIC COMPOUNDS

Chlorophenol tissue residues were better related statistically to the unnormalized bottom water contaminant concentration than with sedi-

ments. The superiority of the residue relationships between fish and bottom water suggests that the principal route of exposure is from the dissolved phase in the water rather than from sediment bound phases. Since these compounds ionize in water, the sediment components that control the availability of metals, such as organic matter, sulphides and Fe/Mn hydroxides would also influence the availability of the ionized species. However, since these compounds generally do not persist in sediments, with the exception of the highly chlorinated species, the sediment concentrations, even in areas of known discharges, are low.

No predictable relationship was obtained between PCB and organochlorine pesticide sediment concentrations and tissue residues. Areas where sediment PCB concentrations were high did not necessarily have high tissue residues in benthic organisms (Appendix, Table 9). Organochlorine pesticide, PCB and chloroaromatic residues in tissues were poorly correlated with bottom water and sediment concentration in both fish and benthos. While the data suggests that sediment concentrations were not a good predictor of tissue residues, the same cannot be said for bottom water or interstitial water concentrations, since the concentrations of contaminants were usually at or below the detection limits and exhibited little or no variability in the data. The often cited belief that exposure to contaminants in the water (water column or interstitial water) is the principal route of uptake by aquatic organisms can neither be proved nor disproved by this study, but must remain as a possible route given the poor correlations between sediment concentrations and tissue residues observed in this study.

In contrast to the other organic compounds, PAH residues in benthos, and to a lesser extent, in fish, were correlated with sediment concentrations, with lipid normalization of residues and TOC normalization of the sediments providing the best results. Numerous studies have shown that the availability of PAHs is related to the sediment concentration, though some of these studies (McElroy *et al.* 1989) have suggested that the actual mechanism of uptake may be through sediment desorption to interstitial water. The same studies have also indicated that fish may acquire at least some of their body-burden through consumption of contaminated prey items. In addition, the relatively weaker relationship between fish residues and sediment concentrations may be due in part to the ability of fish to metabolize many of the PAH compounds (McElroy *et al.* 1989). Only a few

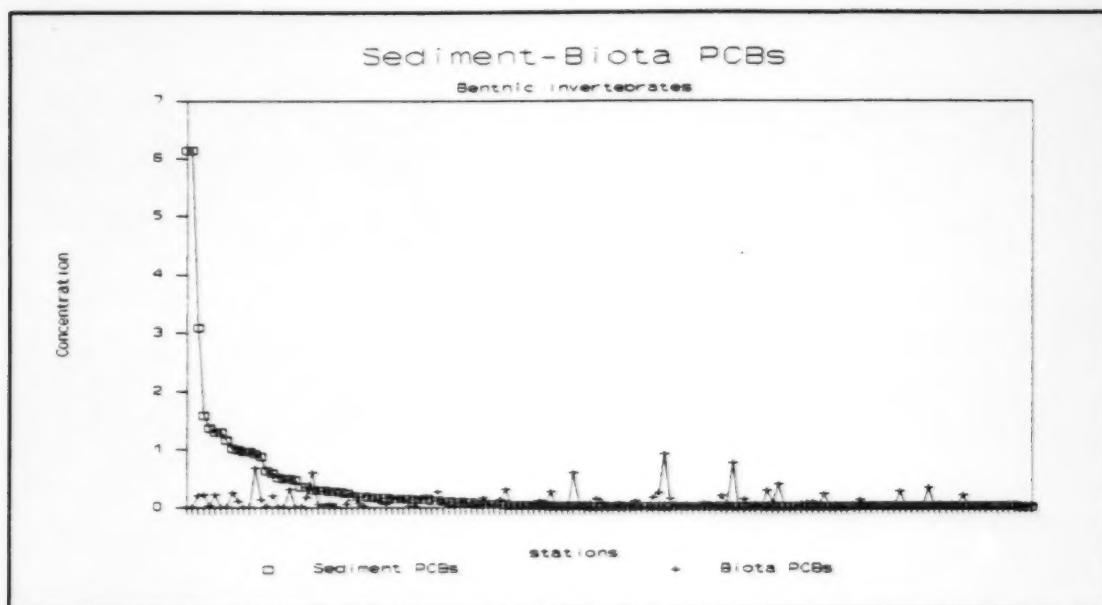


Figure 18: PCB concentrations in sediments and benthic invertebrates (plotted on order of decreasing sediment concentrations). Sediment concentrations in ug/g dry weight of sediment, tissue concentrations in ug/g wet weight of organisms.

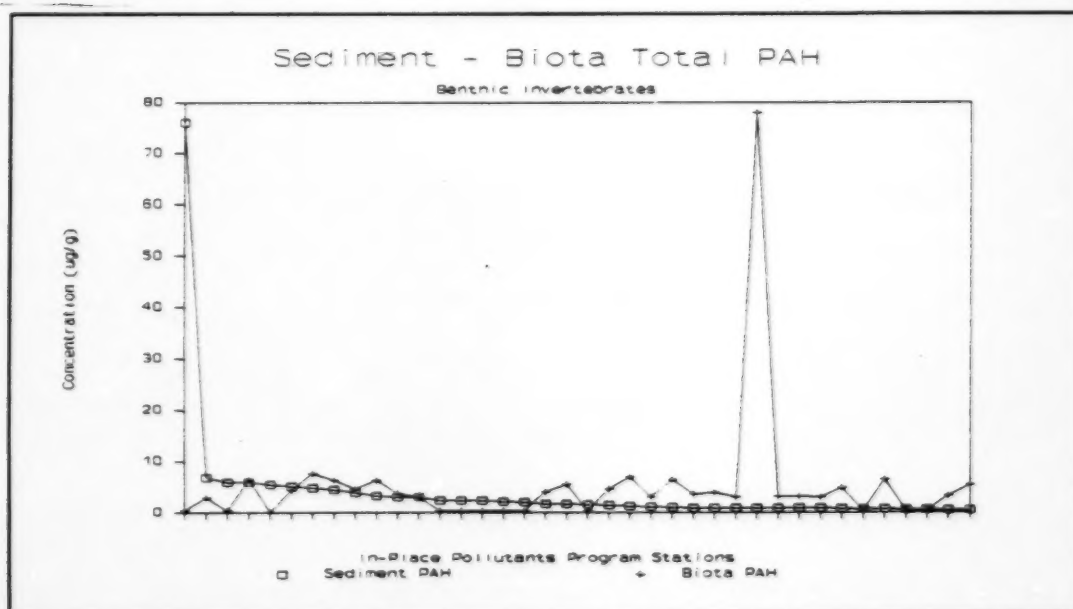


Figure 19: Total PAH concentrations in sediments and benthic invertebrates (plotted in order of decreasing sediment concentration). Sediment concentrations in ug/g dry weight, tissue concentrations in ug/g wet weight.

invertebrates have been suggested as having similar capabilities.

The elevated tissue residues of organic compounds, particularly the PCBs and PAHs at some of the IPP stations, despite low sediment levels, indicates that availability from these sediments is high (Appendix, Tables 9 and 10). Bioaccumulation of these compounds seems to be due primarily to availability from the sediments, which in turn is governed by their solubility and fugacity (the tendency of a compound to leave one compartment and move to another). Literature to date indicates that sorption of these compounds is primarily from the dissolved phase and that sediments act as either reservoirs for desorption to the water phase (McElroy *et al.* 1989; Smith *et al.* 1988) or as sinks. Desorption from the sediment solid phases would tend to result in increased concentrations in the interstitial water, increasing the potential for biological uptake. The low tissue residues in areas of high contamination, such as the Otonabee River and Ashbridges Bay, suggests that desorption from the sediment solid phases does not occur as readily as at those stations outside of these impacted areas. The primary difference between areas where tissue residues are high accumulation and those where tissue residues are low has consistently been the level of sediment organic matter. Sediment organic matter appears to bind these compounds (PCBs, PAHs and the organochlorine pesticides), effectively reducing their availability.

In large measure, the availability of organic compounds from sediment depends on how tightly they are held by the sediment components, a factor which varies according to the compound. Generally, K_{ow} 's have been used to determine the binding strength. However, as pointed out earlier, it has been found that availability is not linearly related to K_{ow} .

Despite the multiplicity of feeding strategies among the benthic organisms, as well as among the fish, there did not appear to be any substantial differences in residue relationships. Generally, patterns of accumulation were similar in all of the organisms tested. The analysis suggests that uptake is primarily dependent on the availability of the contaminant from the sediments or water and that uptake is independent of the feeding strategy or life history of the organisms. This suggests that the general principles of availability from the sediments and water phases determine organism body burdens, rather than individual differences in exposure potential.

The absence of food chain effects between benthos and sculpins cannot be considered as significant given the covariance of residue detection limits, especially for the organics.

Based on the IPP data, the contribution of sediment-bound contaminants to elevated organism tissue residues cannot be quantified. There is strong evidence that they contribute to an organism's body burdens, but that tissue residues depend on a number of factors, which includes water sources and food sources. The relatively low contaminant concentrations in organisms at those locations where sediment concentrations were high and in some cases the very high tissue residues (especially as measured by the BSCR) at those stations where sediment concentrations were low suggests a number of pathways: 1) *sediments are primarily a sink but that under certain circumstances act as a source*; 2) *availability from the sediments is highly dependent on specific features (physical or chemical) of the sediments and the chemical, and*; 3) *availability is primarily from the dissolved phase in the water and interstitial water*. Sediments can therefore affect organisms directly through ingestion of sediment or contaminated prey, and indirectly, through desorption to interstitial water or the water column. Since it was not possible to separate the effects of the water column and interstitial water from the sediments, this problem cannot be resolved on the basis of this study.

5. Laboratory Sediment Bioassays

5.1 Theoretical Considerations

The assessment of sediment by laboratory toxicity tests is generally an outgrowth of the extensive laboratory testing of water that has formed much of the basis of water quality guidelines. As noted earlier in this document, the water column is in some ways a simpler environment than the sediments. As a result, protocols for the testing of water samples for toxic response in aquatic organisms have been well established. The same is not true for sediment testing. Bioassay procedures for sediment toxicity testing are only now being developed and evaluated. All the methods proposed, however, are based on the premise that the effects on a small number of test organisms are representative of the effects on the larger community. As is evident from the previous discussion, this may not always be the case. Sensitivity of the test organisms

may vary, depending on the chemical being tested. The sediment, as noted, plays a critical role in the availability of contaminants and the properties of the contaminant itself significantly affect the sorption chemistry of the contaminant in sediments.

Sediment bioassay testing usually falls into two major categories: testing of field-collected sediments, and testing of artificial sediments spiked with a known quantity of contaminant. Both have advantages and disadvantages. Field testing can be used to determine the toxicity of contaminants in a natural sediment that have been subjected to natural biogeochemical processes. However, in most field situations, contaminants do not occur singly nor are all the contaminants always known (it is impossible to analyze for all of the possible contaminants). Thus, in field collected samples it is usually not possible to establish a cause effect relationship between a specific contaminant and a biological response.

The level of disturbance of the sediment can affect the release of contaminants. As the weight of evidence has shown, the water phase and not the sediment-bound phase is generally the most available and usually the most toxic. By altering sediment redox, pH, and the partitioning of a compound between the sediment and porewater, the availability of a compound for desorption can be significantly altered.

The solution to this has always been the use of spiked bioassays. A "typical" sediment (i.e. a natural, uncontaminated sediment, or one artificially constructed) is used to which is added a known quantity of contaminant. The response of aquatic organisms to this concentration is then measured.

While the tests appear superficially to be simple, there is little agreement regarding the most appropriate tests. Because sediment is a complex medium, composed of organic matter, mineral particles and water there has been difficulty in reaching agreement on which phases are the most appropriate for testing. Four different methods have been proposed, based on different sediment phases: elutriates, porewater extracts, whole sediment and sediment extracts. These are briefly described below.

Elutriates - Sediment elutriation results in the removal of those contaminants that can be removed from the sediment through mixing with water (generally a vigorous mixing procedure is followed). This is followed by filtration to remove particles and

the final aqueous phase is used for the toxicity test. The primary advantage of this procedure is that standard aqueous toxicity tests can be used. The method assumes that the sediment-bound contaminants that are released under normal activities, such as sediment resuspension, have been removed and are in the aqueous phase. Since this phase is the one most commonly associated with toxicity, a strong rationale for using elutriates is provided. The major disadvantages are that the procedure can result in excessive release of contaminants from the sediments due to the mixing procedure and that toxicity due to ingestion of sediment-bound contaminants with subsequent absorption from the gut (which often occurs under mildly acidic conditions) is ignored. The method is most suitable for assessing the effects of sediment release of contaminants on water column organisms.

Porewater extracts- The use of porewater extracts is based on the premise that 1) most of the contaminants that benthic organisms are exposed to are in the porewater, 2) that the aqueous phase is the most available for uptake and the most toxic, and 3) that porewater represents a more natural exposure than elutriates since physical disturbance is kept to a minimum. A number of methods for extracting porewater have been proposed (e.g. Giesy *et al.* 1990), though in all cases it is a water and not a chemical extraction. The disadvantages are similar to those for elutriates, since the assumption is made that the sediment-bound fraction is unavailable and that absorption via the gut is negligible.

Whole sediment - In whole sediment toxicity tests the sediment solid phase is used, either in its entirety as in field collected samples, or it is diluted with other sediments. This has limitations as well, since the porewater is excluded except for what is included in the sample. However, the method does implicitly acknowledge that the sediment solid phases as well as the aqueous phase can contribute to toxicity.

Sediment extracts- In sediment extract tests the sediment contaminants are extracted using any of a number of organic solvents and the extracts are used, without sediment, to assess toxicity (Kwan and Dutka 1990). The advantage is that standard laboratory test organisms for testing water can be used. The rationale for extraction is that the fraction extracted is the easily removed and therefore potentially bioavailable fraction. The use of organic solvents for extraction implicitly, though perhaps obliquely, assumes that the sediment-bound phase can contribute to toxicity, especially though inges-

tion. In reality, the contaminant concentrations that sediment-dwelling organisms may be exposed to are likely to be much lower since the extraction procedure has the ability to remove greater quantities of contaminant than may otherwise be available. The use of extracts in aqueous tests is also likely to expose the test organisms to higher concentrations than would normally be expected.

As noted earlier in section 4, the biological effects of contaminants in sediments have been assessed primarily by inference from the benthic community response and, more recently, by analysis of tissue residues in organisms. Neither provides a direct assessment of the toxicity of the sediment, or the specific causes of the toxicity.

Field bioassay testing provides a direct assessment of the toxicity of a sediment to aquatic organisms. The endpoints (e.g. lethality, reproductive impairment) can be chosen according to the chemical and the biological response being measured or under consideration.

However, there are indications that the sediment tested under laboratory conditions is not directly comparable to field conditions. The toxicity of the sediments can be affected by the test conditions (i.e. agitation of sediment samples prior to testing can result in the release of significantly more contaminant than may be experienced under field conditions). Removal of sediment, particularly anoxic sediment, can result in changes in redox potential with subsequent alteration of partitioning between sediment solids and porewater or changes in the types of complexes formed with sediment constituents. Storage of sediments, both in terms of storage time and storage conditions (e.g., freezing, drying, cold storage) can all change the geochemical properties of the sediment (Swartz 1987).

A major difficulty with all studies using benthic organisms is in separating the effects of sediment contaminants from the effects of the sediment itself (i.e. grain size, organic content) and in some cases mortality may result simply from a sediment being unsuitable for a certain type of organism. In areas where a number of contaminants may co-occur in the sediments it is often difficult to isolate the effects of one contaminant from the effects of all the others.

In the past, much of the effort of toxicity testing

has been directed towards finding the organism that was the most sensitive indicator of a toxicological effect. For a number of reasons this has been supplanted by multi-species testing. Organisms that may be sensitive to one group of contaminants may not be sensitive to others. Variations in sensitivity depend on a number of factors, of which, physiological differences in the organisms and differences in life history, primarily feeding habits and substrate preference, appear to be the major factors.

In most bioassay testing the organism used is a standard test organism that may not necessarily be native to the area sampled. The move to standard test organisms has been undertaken for two main reasons. Because some organisms are particularly difficult to rear for testing purposes the use of standard test organisms ensures a constant supply of organisms that are at a similar age and condition. While the use of standard test organisms also ensures that the results of toxicity test can be compared from one area to another, there are potential pitfalls since it may result in testing of organisms in unsuitable test sediments.

In addition, some organisms may become resistant to certain chemicals through adaption and may not be suitable test organisms (e.g. Keilty and Landrum 1990). Thus selection and collection of organisms for use as test populations must be done carefully.

In an attempt to overcome these limitations, most protocols are now recommending using a number of test organisms in the "battery" of tests approach. A number of different organisms, usually of varying sensitivities and habitats are used. For example, a protocol may use a combination of oligochaete worms, which not only live in the sediment but also consume the fine-particle fraction, a sediment surface dwelling organism, such as chironomid larvae or amphipods, and a water column organism that feeds at the sediment surface, such as certain species of fish.

The endpoints chosen are particularly significant and need to be matched to the aims of the study. In the case of the IPP program, the need was to assess the toxic potential of the sediments in those areas where sediment contaminant concentrations were high.

The biological endpoint to be measured determines the type and duration of the test. Tests conducted to determine rapid lethality of the sediment are relatively short tests. Longer tests, that

expose an organism to the test sediment over a significant portion of its life cycle, or expose the organisms at particularly vulnerable stages in their growth can be used to determine lethality or to assess the more subtle effects that may impair growth and reproduction without affecting the survival of the individual organism. Much longer tests, such as whole life cycle tests that may deduce chronic effects at the population or community level are usually not done, since these require a minimum time of months. This type of assessment is usually better achieved through community structure analysis carried out in the field.

Assessment of in-place pollutants requires as one of its critical steps the assessment of the toxic effects of contaminants on biota. These effects can range from lethality through physiological changes to behavioural changes. While the acute and chronic physiological effects have been well studied, the expression of chronic effects in terms of behavioural changes has received relatively little attention. Drummond and Russom (1990) recorded a number of behavioural changes in fathead minnows as a result of additions of toxic chemicals to the water. Keilty *et al.* (1988) observed changes in burrowing behaviour in oligochaete worms in relation to sediment contaminant levels. Landrum *et al.* (1991) found sediment avoidance in amphipods at higher sediment PAH concentrations.

Toxicity tests can also be conducted to assess the bioaccumulation potential of a compound. Mac *et al.* (1990) found that laboratory results were similar to results from tests conducted in the field (i.e. caged clams, etc)

5.2 Program Synthesis

Sediment toxicity testing, initially based on a protocol to assess the acute toxicity of the sediments over a relatively short time period (10 days) (Lomas and Krantzberg 1988) was begun in 1985. The results of the laboratory tests have generally supported the conclusions of the community structure analysis in terms of the most pronounced effects (e.g., Jaagumagi *et al.* 1990a, 1990b, 1991). In some cases, apparent sediment toxicity was noted in the laboratory, while no apparent effects were observed in the field.

The initial phase of the sediment bioassay program was to develop a protocol to identify those sediments that were acutely toxic. In 1988, Lomas

and Krantzberg published a protocol for an acute toxicity test that was used to assess sediment toxicity for the In-Place Pollutants Program data as well as the MISA Pilot Site Investigations.

The bioassay data served to identify those sediments that were most toxic in terms of potential release of contaminants to the water column. The protocol results in a similar effect to that expected in field conditions where substrates are exposed to disturbance and resuspension. Whole sediment was used in these tests. Toxicity results did not always coincide with the sediment concentrations or the uptake of contaminants by biota in the field. For example toxicity to fathead minnows at the Toronto Main STP site was highest in sediments intermediate in sediment contaminant concentrations (Jaagumagi *et al.* 1991). While these results suggest that release from the sediments was relatively higher than in the more contaminated sediments, the mayfly response did not support this conclusion. It is always possible in such situations that other, unmeasured factors are responsible for the observed effects. These locations however, did not suffer any apparent field effects and the response could not be related to benthic community structure or contaminant uptake. Thus it was very difficult to relate toxicity to any specific parameters of the sediment, or to field conditions. In the few other areas at which toxicity tests were run, the tests generally showed low mortality which could not readily be related to other results. The test procedure, such as agitation, may enhance the availability of contaminants and while no effects are apparent in undisturbed sediment, the bioassays provide an indication of what could be expected if these sediments are disturbed. Note that this is one step better than pure field assessment techniques. The bioassay cannot and will not replace field measurement, but can provide other additional data that may allow the prediction of effects that the field data cannot provide.

The In-Place Pollutants Program identified a strong need for the assessment of more subtle effects on organisms than simply acute lethality. The development of a chronic bioassay protocol was begun in 1985 and through additional research and development by Krantzberg (1990) resulted in a synthesis and evaluation of the available methods. This work has been extended by Bedard *et al.* (1991) and has resulted in a draft protocol for assessment of chronic effects of sediment associated contaminants. The chronic bioassay protocol involves the assessment of contaminants on the long-term health of the organisms by measuring

endpoints such as reproductive and growth impairment.

III. EVALUATION OF THE FINDINGS FROM THE IN-PLACE POLLUTANTS PROGRAM

1. Methods

The In-Place Pollutants program was devised to provide information on the different aquatic compartments that could be affected by contaminants in sediment. The results of the program, as described in the previous sections, have shown that the lack of mechanistic explanations has limited the usefulness of some areas of the study, while emphasizing the importance of others. The results of the different components of the study are reviewed below.

- 1) The difficulty in establishing any correlation between bottom water and sediment concentrations points to the fundamental differences between the two media, (sediments are accumulating material constantly and represent a cumulative record, while water undergoes continuous change) and there appears to be little likelihood correlations between the two media can be established using field-based methods. Because the concentrations in water are generally very low, the statistical analysis is also hampered. In most cases the values were below detection limits and thus not useful for stats. Sediments were not shown to have an effect on water taken one meter off the bottom. Extraction and measurement of sediment porewater would likely be a better measure, since these are more directly influenced by sediments. These could also be more useful in relating toxic effects on the biological components since most of the uptake mechanisms suggest the contaminants in solution, rather than those bound to solid particles, are the main source of toxic effects on organisms.
- 2) Bulk sediment analysis is and will continue to be useful. The bulk values represent the total concentrations of a compound in sediment and provide direct comparison with guidelines (OWDG or PSQGs) for assessment purposes. Bulk sediment results can also be used for comparison among sites and can be an aid in prioritizing other assessment or remedial actions. As well, sediment bulk concentrations can be compared to tissue residues and geochemical fractions (for metals) to determine the movement and potential for adverse biological effects. Finally, they serve as a useful indication of temporal trends in contaminant accumulation if done repeatedly or in a core sample.
- 3) Geochemical analysis of metals in sediment using the extraction scheme described at present provides some additional information above the bulk chemistry though the value of the information relative to the cost will have to be considered in the context of each site. The analysis has shown that there is some relationship between tissue residues and metals in some sediment fraction in some cases. Some of the simpler extraction schemes that have been proposed may offer some promise for greater insight into sediment availability and as result become available, these should be evaluated. The geochemical distribution of metals can also be used as an indication of diagenesis and as an indication of which sediments are of natural origin and which are of anthropogenic origin. As fate and effect models are further refined, the method may have to be refined. However, geochemistry will likely play an important part in some of the models.
- 4) Tissue analysis of benthic organisms has been shown to be a useful measure of sediment contamination since these organisms are generally in direct contact with the sediments. Contaminant analysis of sculpins was found to be less useful than benthic organisms. Sculpins were rarely collected in the same locations as sediment (due to habitat preferences, these fish require mainly hard substrates) and thus there is great difficulty in relating tissue residues to sediment levels. It may be that food serves as a significant source, but this was not demonstrated in any relationship between benthic organism tissue residues and sculpin tissue residues. Mobility of fish, especially in relation to feeding, is also a problem in relating tissue residues to uptake from sediments. As shown in some locations, benthic organisms in areas of sand and gravel sometimes accumulated much higher tissue residues than organisms in soft sediment, even though the latter had considerably higher sediment concentrations of contaminants. Finally, with fish it is difficult to determine the source of the

contaminant since water, sediment and food would all be likely sources. However, the data to date suggests that water could be the major route of uptake. As such, sculpins would be poor indicators of sediment contaminant problems since it appears they measure primarily water column effects. With PAH there is the additional problem of metabolism of the compound. Therefore, while fish provide an excellent means of assessing the biological availability of contaminants in a waterbody, they are unable to provide much insight into the availability of contaminants from specific sources such as the sediments.

Benthic organisms in contrast are much better. Most live in direct contact with the sediment, often ingesting sediment, and so come intimately into contact with sediment contaminants. The major route of uptake in these organisms is likely to be the sediment porewater, which has been shown to differ considerably from the overlying water column.

The use of sediment in-fauna appears to be a more appropriate means of assessing contaminant availability and uptake from sediment, since these organisms are, for the most part, relatively sessile. Their virtually continuous exposure to sediment contaminants through ingestion of the solid phases as well as through surface adsorption from the interstitial water suggests that the contribution of contaminants from the dissolved phase in the water column would be minimal. Thus these organisms have the greatest potential for use as a monitoring or assessment tool for sediment contamination.

5. Benthic enumeration studies have traditionally been relied on for the assessment of contaminant problems in aquatic systems. The response measured is at the population and community level and they are integrators of all the physical and chemical changes that have occurred in the sediment, generally over a period of a number of generations. Thus they essentially measure the long term and often the chronic effects of contaminants. The difficulty lies, as identified above, in distinguishing the response of the benthic community to chemical contaminants from the response to physical features of the environment. The community composition has been shown to be particularly sensitive to changes in the organic content of the sediment, the temperature and the oxygen concentration. Since contaminants generally accumulate in soft sediments high in organic matter, and since this

type of sediment also exerts a strong oxygen stress on the organisms, it is sometimes difficult to determine the exact cause.

As with other methods of biological assessment, it is also not possible to definitively separate water column effects from sediment effects since the benthic community responds to both. As such, it is unsurpassed in its ability to assess the overall biological integrity of a system, since all the physical and chemical effects are integrated by the benthic community and are expressed as a community and functional response. A particular advantage of using benthic organisms is that the effects of other, unmeasured variables are also included in the response, an attribute which is noticeably lacking in the other techniques.

- 6) The In Place Pollutants Program identified the need for the development of sediment bioassay methods and aided in the initial development of what has become an ongoing program. The results have shown that laboratory bioassays can be useful in measuring the effects of sediment contamination on benthic and water column organisms in a more quantitative fashion, considering both the acute effects of high concentrations of contaminants as well as the chronic effects that may result from lower concentrations. Sediment bioassay testing has as a result, become a regular analysis procedure, with facilities in place for routine sediment testing. Even so, certain factors must be considered. Disturbance of the sediment often alters the redox conditions of the sediment during sampling. Storage may change the geochemical nature of the sediment, altering the contaminant availability, while mixing of the sediment (forced aeration) also changes the potential availability of the contaminants. Thus the results from laboratory tests may not accurately reflect natural conditions of the sediment. In all probability the results are likely to overestimate the toxicity of the sediment. Finally, due to the use of field sediment, these tests do not make it possible to determine the chemical or chemicals responsible for the toxic effect, but merely recognizes that an effect is present. In defence, one must recognize that only tests such as spiked bioassays in the laboratory, can determine a direct cause-effect relationship between sediment contaminant levels and organism response. It must be recognized however, that differences in the sediment type, sediment aging effects (diagenesis), oxy-

gen levels, the presence of other contaminants that can have synergistic effects, that may not be accounted for in spiked bioassays.

2. The In-Place Pollutants Program Approach

While taken individually, many components of the program do not appear to offer definitive information on the effects of contaminants in sediments, when taken together a number of these components can serve as means of identifying whether an effect is present and usually can provide some insight into which factors are most likely resulting in an observed effect. Thus, in studies of this type, the effects are drawn mainly by inference. This is a problem common to all studies that utilize field investigation. In effect the program describes a co-occurrence analysis of benthic organisms and sediment chemical conditions.

In many respects it is misleading to simply look at sediments in terms of effects on benthic organisms and communities. This type of analysis also deviates from the intent of the ecosystem approach. By considering only a simple relationship, such as sediment contaminant concentrations and benthic communities, the implicit assumption is that sediments are the only factors affecting the benthic community.

There are no suitable mathematical models or statistical tests to evaluate these relationships because they are so complex, and for the most part, unpredictable. Benthic communities are affected by chemical and physical characteristics of the sediment and the water. The severity of the effects from each can also vary, depending on the behaviour and life history of the organisms. The tendency to use multivariate tests to determine the effects of sediment contamination falls short because of these inter-relationships. While these techniques can be useful in determining patterns, they do not work particularly well at discriminating between the effects of specific contaminants and benthic community response. The problems are further compounded if there is correlation among the various contaminants, and in such cases convincing statistical analysis is impossible (Clarke and Green 1988). This has often been shown to be the case in the In-Place Pollutants study, where contaminant concentrations are closely related to the sediment type, either through sediment organic matter (TOC) or sediment grain size.

The various methods of biological assessment

can be used to independently assess effects, and then to combine them, as a cross-checking procedure. This in effect provides a "weight of evidence" type of interpretation. If, for example, sediment concentrations are high, the benthic community is reduced, and significant bioaccumulation has occurred in those organisms still present, these types of conclusions can be used to link sediment bound contaminants to biological effects. However, these analyses provide little if any insight into the actual mechanisms of the effects.

Thus, in most cases, the connections between sediment contamination and biological responses is mainly by inference. Laboratory bioassay tests, on field collected sediments, can provide a more substantial link between sediment contaminants and biological effects, but the resolving power is limited to simply determining that an effect is present. Where more than one contaminant may be present, this provides little more resolving power than any of the other techniques. In all these cases, an educated guess (inference) is required to link the effects with one or more possible causes. As stated above, this must rely primarily on the "weight of evidence" approach.

Thus it appears there is no simple means of assessing the impacts of contaminants on aquatic life. As such, it is necessary to assemble information from all the different sediment and biological compartments in order to narrow down the search.

However, we do know that sediments can affect bottom water concentrations, benthic organism tissue residues and benthic community structure. These effects have been documented at many of the individual sites studied in the course of the program. What we cannot do is predict the effects of a given sediment concentration of a substance. In large part this is because the effects of sediment-bound contaminants depend on a host of other physical and chemical characteristics of both the sediments and water column.

This is also due to the fact that there is no such thing as a standard or typical sediment. Sediment, by definition, is a collection of minerals and organic debris that has settled to the bottom. Its composition depends on the local geology of the watershed and the various biological inputs, both allochthonous and autochthonous. As such, sediments are extremely variable. Finally, everything that is deposited in the sediments must pass through the water column and sediment composition is therefore also affected by solution chemistry. Even when material is deposi-

ted on the sediments, it is exposed to water, which therefore continues to play an important role.

3. Recommendations for Sediment Sampling Programs

Based on the previous discussion, a number of methods, combined in an integrated approach, can be recommended for the assessment of sediment. Ideally, a detailed site investigation would include an analysis of the bulk sediment chemistry for all contaminants that may be of particular interest within an area, benthic enumeration studies, benthic organism tissue residue analysis and a laboratory bioassay on the sediment, with suitable endpoints.

Additional investigations may also include analysis of porewater for contaminants, particularly to aid in the assessment of contaminant movement to the water column and biota. Where it is deemed necessary, as in areas of high natural background concentrations of metals or in areas receiving significant inputs of metals, geochemical evaluation of the sediment may be added as an option.

The analysis of fish, while an excellent means of assessing contaminant movement and availability within the entire system, do not provide particular insight into sediment availability. However, these would be recommended in any detailed site evaluation on the effects of loadings to the watercourse or waterbody. Similarly, water analysis would be included in a detailed investigation, though in terms of sediment assessment, this offers little additional insight.

IV. FUTURE DIRECTIONS

The In-Place Pollutants Program has shown that because sediments form an integral part of the whole aquatic cycling process, it is not possible to consider sediments in an isolated context. Nor is it possible to separate effects of contaminants in the water column from the effects of contaminants in the sediments using field-based data. While controlled laboratory investigations can break the cycle down into its component parts, these provide little indication of how the process may operate under natural conditions when these components have to interact as part of a more complex whole.

The interrelationships between sediment and the other aquatic compartments are only now being elucidated.

The In-Place Pollutants Program has shown that progress is now required in certain directions in order to answer some of the questions still left unanswered. These are necessary if sediment contaminant problems are to be addressed in a regulatory context.

1. There is a need to develop a close relationship with laboratory bioassay testing to determine the mechanisms by which contaminants are sorbed and affect aquatic organisms.
2. Development of mechanistic models to determine the movement of contaminants once these relationships have been quantified (if ever).
3. The In-Place Pollutants program has highlighted the need to develop a standard protocol by which we can assess field conditions and measure these in relation to other areas with sediment contaminant problems. This means a standard series of assessment procedures, of which section III (3) is the beginning, by which we can gather acceptable "weight of evidence" data.
4. Inherent in the assessment of existing conditions is the need then to identify those areas that are "clean" and devise criteria for remediation (i.e. what do we clean up to?). Can the IPP Program provide a suitable target in ecological terms that we should strive for? The development of sediment quality criteria represents the first efforts in this direction.

The In-Place Pollutants Program has shown that the integrated, "weight of evidence" approach provides the only effective means of assessing the effects of contaminated sediments. By highlighting the complex interactions of sediments with both the water column and the sediment-dwelling organisms, it has shown that a number of assessment techniques are required to provide the types of information needed to assess biological impacts and to guide management action. The program has also shown that it is impossible at this stage of our understanding of the mechanics of contaminant action in sediments, to rely for detailed assessment on any one single technique. Information is required from a number of sources to provide sufficient "weight of evidence". As such the program has highlighted the need for similar assessments of

sediment quality on a broader scale than was possible in the short life-span of the program. In particular, the methods would be suitable for monitoring programs developed on a watershed scale. There is a strong need for adoption of an In-Place Pollutants monitoring program that follows an ecosystem approach as recommended by the IJC as a basic tool of environmental quality assessment.

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